Density Functional study of graphene on insulating substrates

by

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Density Functional study of graphene on insulating substrates

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I am eternally grateful to my mother for being such a brilliant source of inspiration in my life. The force of encouragement and the voice of reason behind all my achievements, big or small, she has indeed been my true friend, philosopher and guide.

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Abstract

Density Functional study of graphene on insulating substrates

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The University of Texas at Austin, 2009

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Abstract: This is a study of the structural and electronic behavior and properties of graphene on α-quartz and α-sapphire using Density Functional Theory. We construct initial structures using the above 2 substrates, place a layer of graphene on them and subsequently allow the atoms to relax. After relaxation we study any structural changes, band structures, density of states, charge density to determine the electronic properties of the entire structure. Eventually this study will help in the search for good substrates for graphene based transistors.

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Chapter 1: Introduction

This study attempts to simulate and understand the behavior and properties of graphene on new substrates. We aim to comprehend the structural and electronic properties of graphene on α-quartz and α-sapphire using Density Functional Theory (DFT).

Graphene as we all know is a single atom thick sheet of carbon atoms arranged in a hexagonal lattice. These carbon atoms are bonded to each other via sigma bonds between sp^2 hybridised C orbitals. Owing to its unique structure and properties, graphene has generated incredible interest in the scientific community. In particular, graphene is expected to show linear dispersion and zero band gap, high mobility of carriers and subsequently high conductivity and high spin relaxation lengths. All these properties make graphene a highly desirable channel for charge or spin conduction purposes.

In an attempt to harness its high mobility, researchers are trying to use graphene as a channel in a Field Effect Transistor (FET). We are currently working on a design of a Spin Field Effect Transistor (SPIN-FET)-which has a spin polarized current in place of a charge based current). We intend to incorporate graphene as a channel in this SPINFET in order to make use of its potential to conduct spin currents. It is in relation to both these attempts that we are, as a first step, trying to obtain a better understanding of graphene on a substrate. While that is our motivation, our present study is more general and is valuable even as an independent look into the behavior of graphene on substrates.

For our purposes we have chosen α-quartz and α-sapphire as the two substrates on which we shall place graphene. While quartz (SiO_2) is a most natural choice for a substrate given its extensive use in the semiconductor industry, we choose α-quartz since it is the most common polymorph of silica (SiO_2). Similarly sapphire is also a very

commonly used substrate is the industry. In addition to this, both quartz and sapphire crystals can be cut to yield hexagonal surfaces with lattice constants that match quite well with graphene, as we shall see later. Additionally they are insulating and thus all in all promise to be good, non-interfering substrates for graphene.

THEORETICAL METHOD:

To study the above structures we use Density Functional Theory (DFT). We give a brief sketch of the framework of this particular theory. To begin with, as we know, the behavior of any quantum system is governed by Schrodinger's equation. For a collection of various nuclei and electrons in equilibrium, that constitutes a unit cell of our structure, the time independent Schrodinger's equation can be written as follows:

$$\mathcal{H} = -\sum_{I=1}^{P}\frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_{i=1}^{N}\frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{2}\sum_{I=1}^{P}\sum_{J\neq I}^{P}\frac{Z_I Z_J}{|R_I - R_J|} + \frac{e^2}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|r_i - r_j|} - e^2\sum_{I=1}^{P}\sum_{i=1}^{N}\frac{Z_I}{|R_I - r_j|}$$

Here M_I is mass of I^{th} nuclei, m is mass of an electron, e is charge of an electron, Z_I is charge on I^{th} nuclei, r_i is position of i^{th} electron and R_I is position of I^{th} nuclei.

Eigenvectors of this Hamiltonian will yield the stationary states that these constituent electrons and nuclei would like to occupy in our system. While this Hamiltonian is easy to write analytically it is virtually impossible to solve for a sizeable collection of atoms. There are various degrees of complications involved in exactly solving the Hamiltonian and physicists employ a host of approximations to deal with them.

First we notice that the Hamiltonian above is written in terms of nuclear as well as electronic coordinates and has nuclear-electron interaction terms. This complicates matters in that the Hamiltonian is no longer separable into separate nuclear and electronic wavefunctions. However it is frequently the case that nuclei are much slower than electrons, so much so that the movement of nuclei does not perturb electronic eigenstates or cause electronic transitions. This is called the Adiabatic Approximation and it allows us to write the total wavefunction as a product of the electronic and nuclear wavefunctions, thus separating the two.

In addition it can be argued that if inter-nuclear distance is much greater than the thermal wavelength of nuclei, there is no phase coherence between the nuclei and if we neglect inter-nuclear forces, we can treat the nuclei as classical particles for all practical purposes. This is called the Classical Nuclei Approximation. This enables us to write nuclear coordinates in a classical form, thereby further simplifying our problem.

Now we have obtained a Schrodinger's equation for electronic wavefunctions that has a kinetic energy term, a nuclear-electronic interaction potential and an electron-electron interaction potential.

$$\mathcal{H} = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 - e^2 \sum_{I=1}^{P} \sum_{i=1}^{N} \frac{Z_I}{|R_I - r_j|} + \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|r_i - r_j|}$$

Solving for this Hamiltonian is not easy either since here we have a Coulombic two electron interaction which turns this into a many body problem. Thus, we cannot write the solution in terms of independent electronic wave functions or their products. In addition, the entire wavefunction has to be anti-symmetric under exchange of electrons (because they are fermions) in order to satisfy the Pauli exclusion principle. So this is an inseparable partial differential equation in 3N variables.

Further simplifications are thus required before one can attempt this problem. The purely classical, non-correlated part of the electron-electron Coulombic potential is extracted and it constitutes what is known as the Hartree term. This is what the electron interaction would have looked like if we had a purely classical system with no correlations between electrons. The remaining term is called the correlation term. The exchange term of the Hamiltonian can also be added to this correlation term in which case it becomes the exchange-correlation energy term. The exchange term, as mentioned before comes from the fact that the total wavefunction has to be asymmetric with respect to exchange of electrons.

So now the main complications are arising from the exchange correlation part of the Hamiltonian because it is a many body term and is computationally prohibitive to calculate. There are various methods employed to get around this. Density Functional Theory is one of them.

Around 1928 L.H. Thomas and E. Fermi proposed that the full electron density was the fundamental variable of this many-body problem. From this idea they derived a differential equation for the density without using electronic orbitals. Later Hohenberg and Kohn proved that the total electronic energy including the kinetic, exchange and correlation terms, could be written in terms of the electronic density. In fact they went on to prove that the electronic density unequivocally determines the ground state wave function of the electrons.

It seemed like once they could get the correct electronic density, the problem was solved. There was still the issue of dealing with the many body interaction terms. Kinetic energy, even though easiest to write down, is a non-local term. To simplify it, Kohn & Sham proposed that if one could find a system of non-interacting electrons with the same density as that of the interacting system, the kinetic energy of the non-interacting system

would be a first approximation to the kinetic energy of the interacting system. Once we use this first approximation the missing terms would be an exchange and a correlation term in the kinetic energy. These missing terms could then be grouped with the exchange correlation potential term after substituting for the kinetic energy from a non-interacting system.

Following their prescription, we have the entire complicated many-body part of our problem contained in the exchange-correlation energy term. This term may be a small correction. The idea now is to look for suitable approximations for this term. There are various schemes that carry out this approximation, the two most popular amongst them being the Local Density Approximation (LDA) and the Generalised Gradient Approximation (GGA).

The LDA considers an inhomogeneous electronic system as locally homogeneous and then uses the exchange-correlation corresponding to the homogeneous electron gas as a substitute. LDA is quite successful with systems that have quite uniform electronic density. To address the issue of in-homogeneities in the electronic density, we write the exchange correlation part in terms of the gradient of electronic density apart from the density itself. This scheme, called GGA, can capture some short range effects.

With the above formalism of DFT, or minor variations of it in place, we are now equipped to solve for the electronic density and wave functions in a self consistent manner to get solutions to Schrodinger's equations.

Chapter 2: Graphene : Monolayer and Bilayer

This work is a study of the effect of various substrates on a single layer of graphene. We create a structure constituting a graphene mono-layer placed on a section of the desired substrate and study its properties. We hope to find a substrate which opens up a small gap in the band structure of graphene layer without altering its linearity too much. In case we see that the mono-layer of graphene is getting severely affected by the underlying substrate, we shall go onto study bi-layer graphene on substrates, treating the first layer as a buffer. In this context we first take a look at the properties of suspended mono and bi-layer graphene.

BANDSTRUCTURE OF SUSPENDED GRAPHENE:

In addition to the above motivation we wanted to make basic checks to our DFT code to see if it was giving expected results. So we ran simulations for mono and bi-layer graphene to get its bandstructure and the results are shown below:

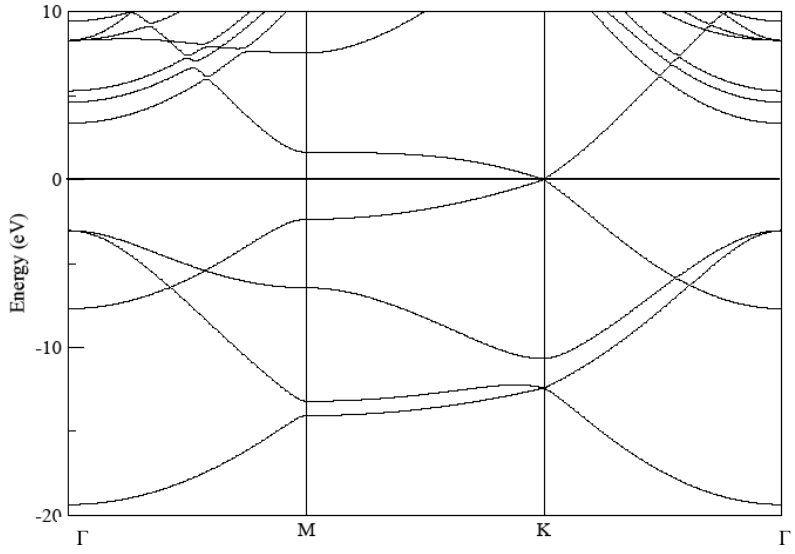


Figure 1: Band structure of mono-layer graphene. Fermi energy is at 0eV.

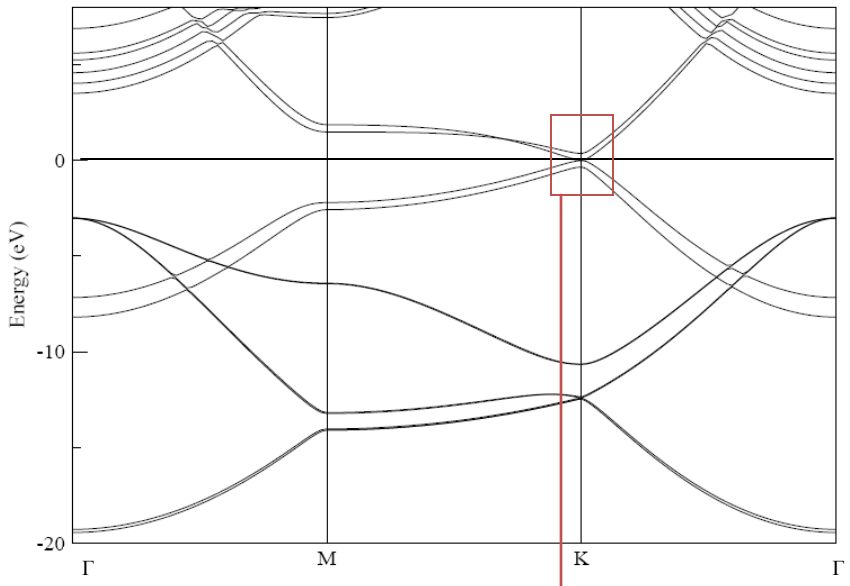


Figure 2 (a): Band structure of bi-layer graphene. Fermi energy is at 0 eV.

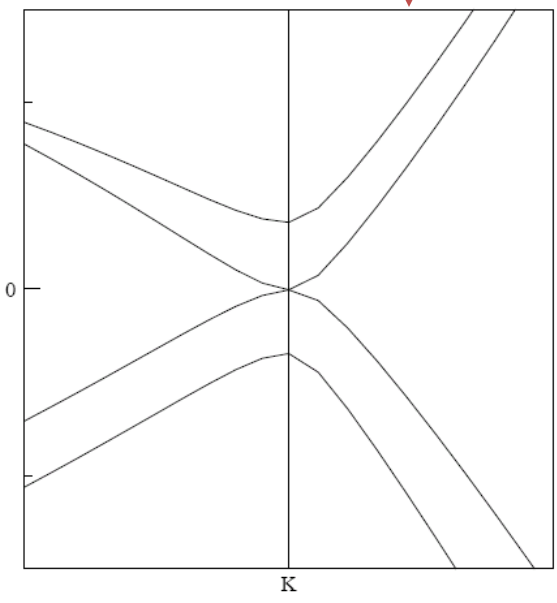


Figure 2 (b): Band structure shown in Fig 2(a) zoomed in. Fermi energy is at 0 eV. Note there is no gap at K point.

Notice the linearity of the band structure and the zero gap at the Fermi energy which is characteristic behavior of graphene.

DETAILS OF CALCULATIONS:

We conducted our DFT calculations using the program Vienna Ab-Initio Simulation Package (VASP). In our simulations we used energy cut-off for the plane wave basis set as 612.2564 eV, desired energy accuracy for self consistency as 1E -5 eV, a 7x7x1 mesh for K points and LDA based Projected Augmented Wave (PAW) pseudopotentials for exchange-correlation approximation. These computational parameters were chosen in order to achieve good convergence criteria for the system.

In order to relax the ionic positions, starting structures were provided and some of the atoms were marked out so as to allow their x, y and z coordinates to change without changing the lattice constants of the entire unit cell. The program then moved these atoms in small steps using a conjugated-gradient algorithm. For each such step, called an ionic iteration, the Schrodinger's equation is solved self consistently to get new electron densities and Hellman-Feynman forces, using Kohn-Sham wave functions, are calculated on each atom. If each of these forces is less than the prescribed value, given by us, then the relaxation is said to have converged. Else the self consistent loop is iterated until the ionic convergence is achieved. For these calculations we specified a force cut off of 0.01 eV/Å for each component.

Chapter 3: Substrates for graphene growth

We study two different substrates in this study, namely α-quartz and α-sapphire. α-quartz is a crystalline form of SiO_2 and α-sapphire is a crystalline form of Al_2O_3, both are naturally occurring minerals on earth.

SECTION: STRUCTURE OF SUBSTRATES

α-Quartz:

α-Quartz has hexagonal symmetry with the following lattice constants:

a= b = 4.913Å & c = 5.4053 Å. The angles being: α =β=90^o, γ=120^o. Below is a figure depicting one unit cell of this substrate.

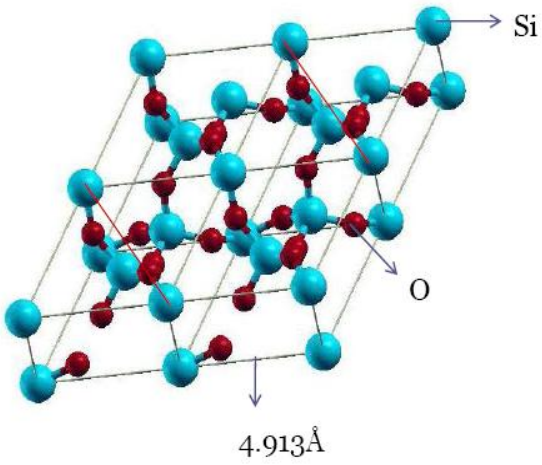


Figure 3: Structure of bulk α-quartz.

α-Sapphire:

α-Sapphire has Rhombohedral Crystal Symmetry with a=5.128Å and α = 55.287°. When we try to construct a hexagonal cell from the rhombohedral one, we do not get a perfect hexagon. Instead we obtain a=5.128Å, b = 4.758Å and α=55.287°. Since we want to fit graphene onto the substrate we take an average of a and b such that: a = b = 4.943Å and α=60°, c = 4.9075Å. Below is a figure depicting one unit cell of this substrate.

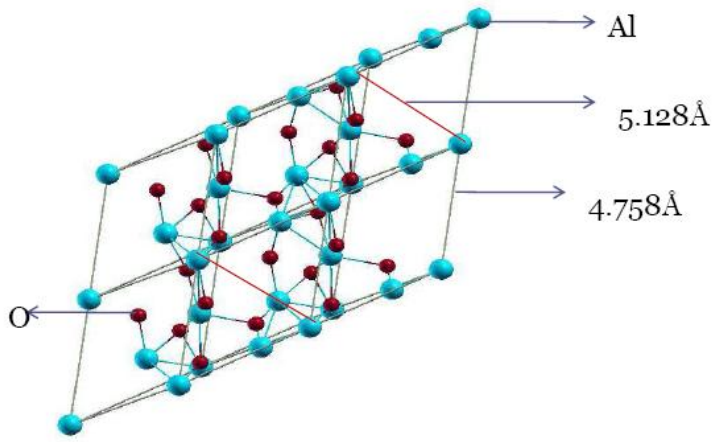


Figure 4: Structure of bulk α-sapphire.

OPTIMISATION OF LATTICE CONSTANTS:

Thus we started out with the bulk structure as described in literature and subsequently relaxed the lattice constants a and c to find the optimized structure with minimum energy as prescribed by DFT. The relaxation of lattice constants was carried out between -3% to +3% of their experimental value using both LDA as well as GGA.

Quartz:

Experimental values of lattice constants were: a = 4.9134Å c/a = 1.10009

LDA gave: a =4.91405Å c/a 1.10045

GGA gave: a = 4.9786Å c/a = 1.099376

LDA was extremely close to the experimental values of a and c. Thus to build future structures we used these LDA values and for further calculations used the LDA pseudopotential.

Sapphire:

Experimental values of the lattice constants were: a = 4.943Å, c = 4.9075Å

LDA gave: a=4.90731Å c = 4.907712Å

GGA gave: a=4.9854Å c = 4.90816Å

Both the values are pretty close, we took LDA as the approximation for the exchange correlation and used the lattice constant values given by LDA.

Chapter 4: Graphene on Substrates

GRAPHENE ON QUARTZ (INITIAL STRUCTURE):

We built a hexagonal cell from quartz (100) and compared it with the hexagonal crystal structure of graphene. The C-C bond length in graphene is 1.421 Å.

a(hex Qz) = 4.913*√3 = 8.510Å

a(hex Gr) = 1.421*2*3 = 8.526Å

There is a mismatch of 0.19% between the two which is pretty small. quartz thus seems to be a good substrate for graphene.

Below we depict a schematic of 1 layer of graphene on 10 unit cells of hexagonal quartz. There is 1nm of vacuum. The distance between the top most Si layer and the graphene layer is taken as the average bond length of SiC= 1.61Å. We passivate the lower Si surface with 2 hydrogens per Si atom.

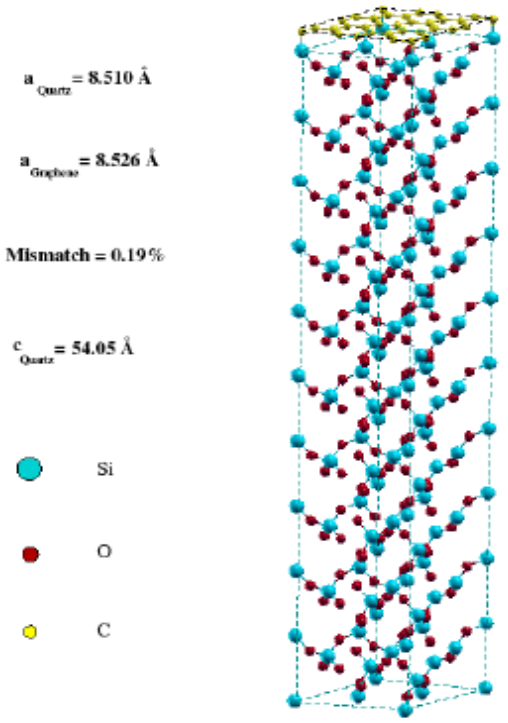


Figure 5: Graphene mono-layer on 10 unit cells of quartz.

GRAPHENE ON SAPPHIRE (INITIAL STRUCTURE):

We built an averaged hexagonal cell from sapphire (100) and compared it with the crystal structure of a layer of graphene. We found that:

$a_{(hex\ Sp)} = 4.943*sqrt(3) = 8.562Å$

$a_{(hex\ Gr)} = 1.421*2*3 = 8.526Å$

Thus the mismatch between the two lattice constants is 0.42%.

Below we include a schematic of 1 layer of graphene on 4 unit cells of hexagonal sapphire. There we have 1nm of vacuum. The distance between the top most layer of Al on substrate and the graphene layer above it is taken as the average Al-C bond length in Al_4C_3 i.e. 1.93Å. We passivate the lower Si surface with 3 H's per Si atom.

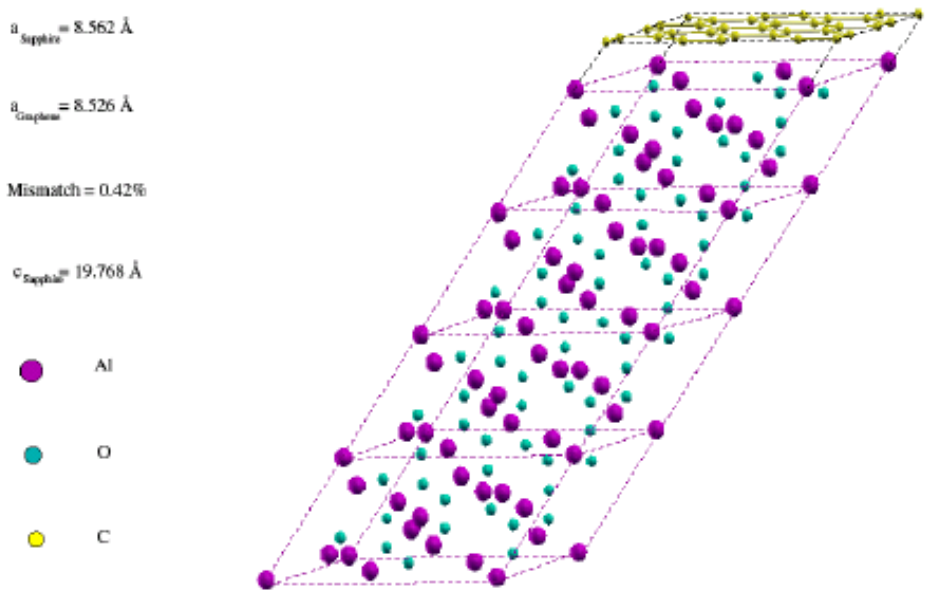


Figure 6: Graphene mono-layer on 4 unit cells of sapphire.

FINAL STRUCTURE AFTER RELAXATION:

In our calculations we take 5 unit cells of substrate with 1 layer of graphene and relax all coordinates of atoms in the top 2 unit cells of the substrate and the graphene layer.

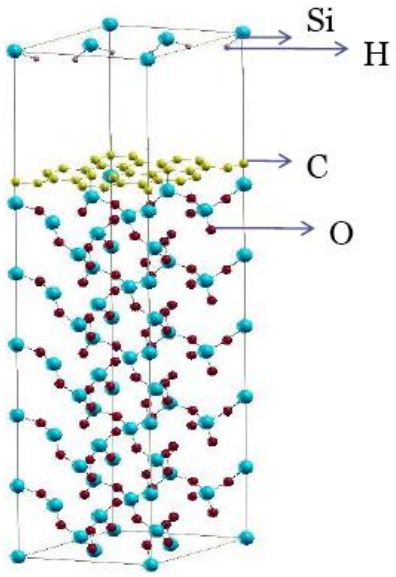


Figure 7: Initial structure of graphene on quartz before relaxation.

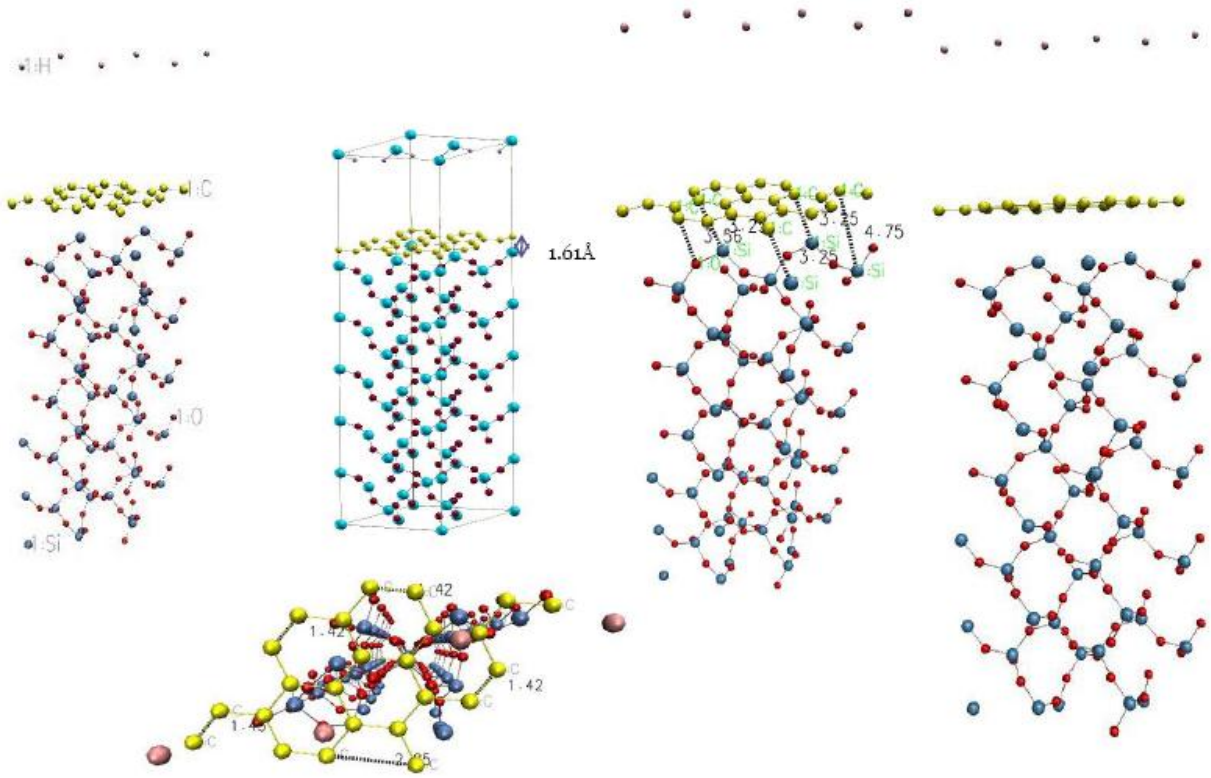


Figure 8: Final structure of graphene on quartz after relaxation.

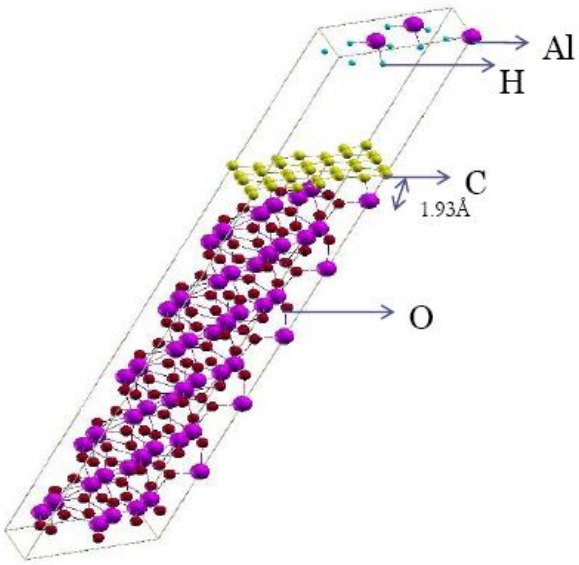


Figure 9: Initial structure of graphene on sapphire before relaxation.

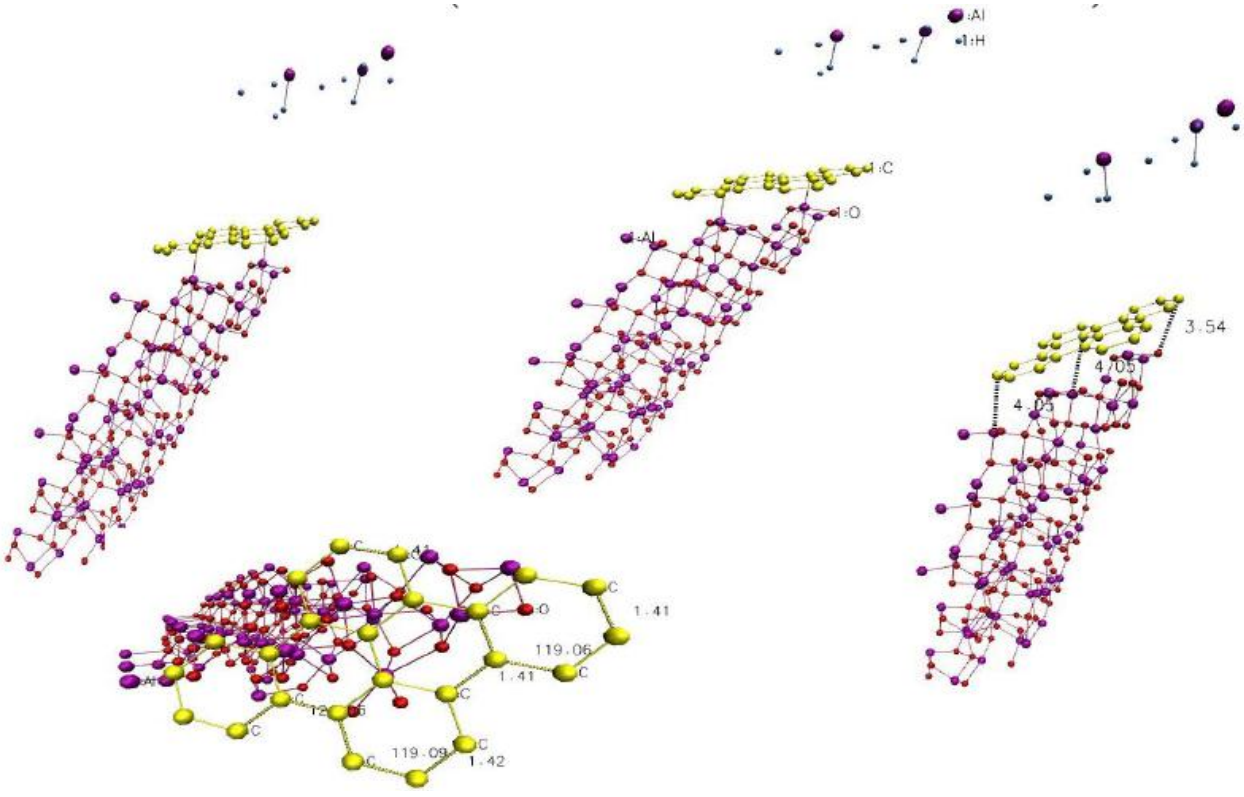


Figure 10: Final structure of graphene on sapphire after relaxation.

STRUCTURAL ANALYSIS:

We will now describe the analysis of positions of atoms that were allowed to relax in our structure.

Graphene on α-quartz:

Silicon:

There are 21 atoms of silicon within the 2 unit cells of our substrate that are allowed to relax. We observe a regular pattern of movement along the z axis (c lattice vector) with all displacements being negative. This means that the Si atoms are pushed into the substrate, away from graphene. In general, the atoms move by small amounts.

In the top 2 unit cells (allowed to move), there are 7 planes of Si atoms. The first plane of atoms moves from a height of 27.05Å to 26.6 Å i.e. it is pushed below by 0.45 Å. Eventually the top most Si layer is at an average distance of 3.00 Å from the graphene layer. The next plane is pushed below by 0.16 Å. The displacement reduces as we go away from graphene till the lower most mobile plane is moved only by 0.015 Å.

Oxygen:

There are 12 planes of oxygen within the 2 substrate unit cells in our structure that are allowed to move. Along the z axis, the displacements are alternate in modulus. The first plane is moved from a height of 26.4 Å to 26.1 Å, i.e. by 0.218 Å below. It is finally at an average distance of 3.4161 Å from the graphene layer.

The other 11 planes also get displaced by -0.2 to +0.04 Å The displacement spreads in a zigzag fashion (increasing and decreasing alternately as we go to lower planes). But on an average this displacement decreases.

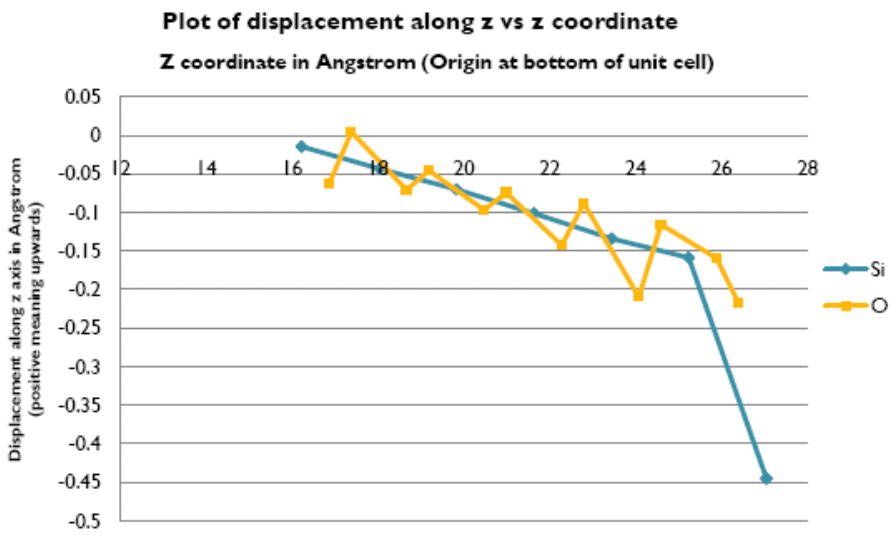


Figure 11: Plot of displacement of z coordinates of Si and O atoms in quartz.

Carbon atoms:

There are 24 C atoms in the graphene layer in our unit cell. The final average height is 29.60 Å from base of the unit cell. This means that the graphene sheet has been pushed up by an average of 0.946 Å away from the substrate to a final average distance of 3.00 Å from the top most Si layer. The standard deviation in height of C atoms is 0.044 Å which points towards an effectively flat surface.

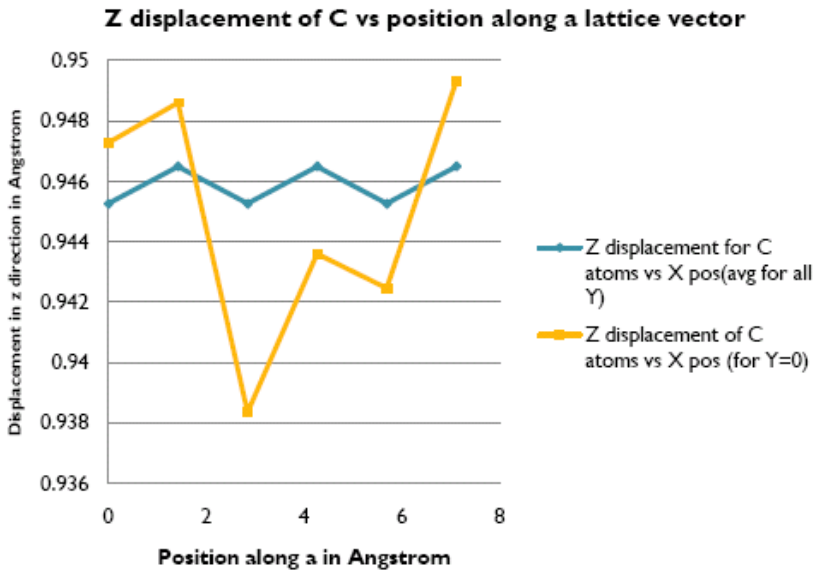


Figure 12: Plot of displacement of z coordinates of graphene C atoms.

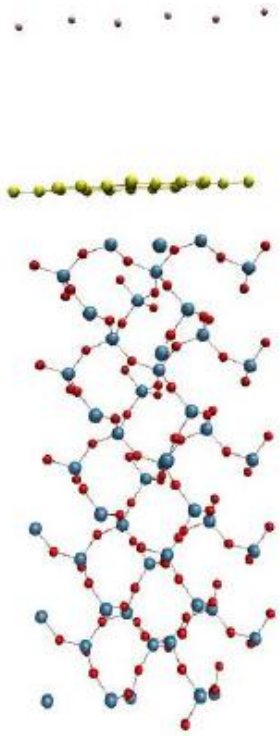


Figure 13: A side view of the final structure showing the flatness of graphene layer.

Graphene on α-sapphire:

Aluminium atoms:

There are 9 planes of Aluminium atoms in the 2 unit cells of substrate allowed to relax in our structure. Each of these planes has 3 Al atoms and within each plane the final displacements differ a little (generally by orders of a few hundredths of an angstrom).

Along the c axis all displacements are negative. Al atoms are pushed down closer to the base of the substrate away from graphene. The displacement of the top most layer is around 0.28 Å, while that of the next layer is 0.37 Å. The displacements have a zigzag pattern i.e. they increase and decrease alternately for adjacent planes. However on the whole they decrease to 0.06 Angstrom for the lowest moving plane.

Oxygen atoms:

There are 12 planes of O atoms in the 2 unit cells of sapphire that we allow to move. Again the displacement of O atoms belonging to the same initial plane along the c axis is similar but not the same. We should recall here that the structure we are using for sapphire was an approximation of the actual sapphire structure to begin with. Again all displacement along the c axis are negative as all O atoms are pushed down away from graphene. The first plane is displaced by just as much distance as the first plane of Al atoms i.e. by around 0.29 Å. After this the pattern looks zigzag, On the whole, the displacement decreases as we go from the top most plane to the bottom most moving plane. For the bottom most moving plane the displacement is very small, about 0.01 Å.

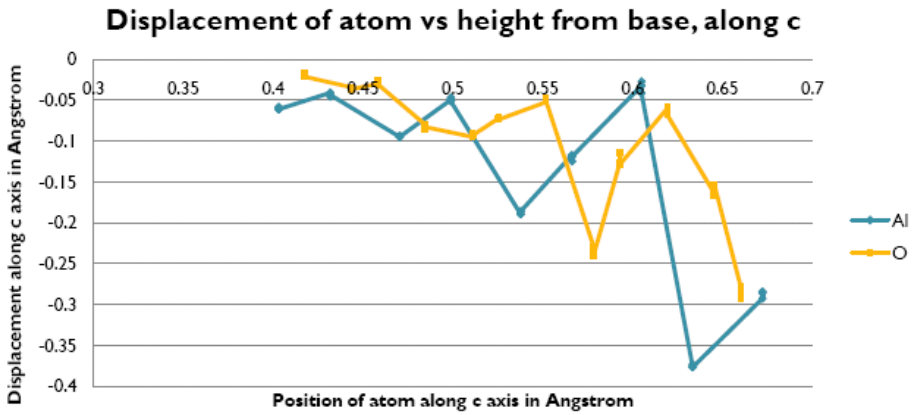


Figure 14: Plot of displacement of Al and O atoms in sapphire along c.

Carbon atoms:

There are 24 C atoms in the graphene layer in our unit cell. Unlike for quartz the final C atoms sheet is distorted here so we need to calculate average shifts and standard displacements.

Along the c lattice vector, all displacements along c are positive which means the graphene sheet is being pushed up and away from the substrate. The individual shifts differ with atoms but the average shift is 0.4636 Å and the standard deviation is 0.04396Å. Finally the distance between the top most Al layer and the graphene sheet is 2.7 Å.

The above analysis gives us a clue about the effect of quartz and sapphire on the graphene layer. In both cases the graphene layer is pushed away from the substrate we expect there to be very little bonding between the two, if any. As a direct consequence we don't expect too much perturbation by the substrate to the band structure of the graphene layer.

Chapter 5: Graphene-on-substrate Band Structures

We have already seen the band structure of mono and bi-layer graphene. We shall now calculate using DFT and study, the band structures of bulk substrate and also our final relaxed graphene on substrate structures.

BAND STRUCTURE OF BULK SUBSTRATES:

Bulk α-quartz:

We first obtained the band structure for bulk quartz (which is shown below) and then compared it with band structure of α-quartz as described in literature.

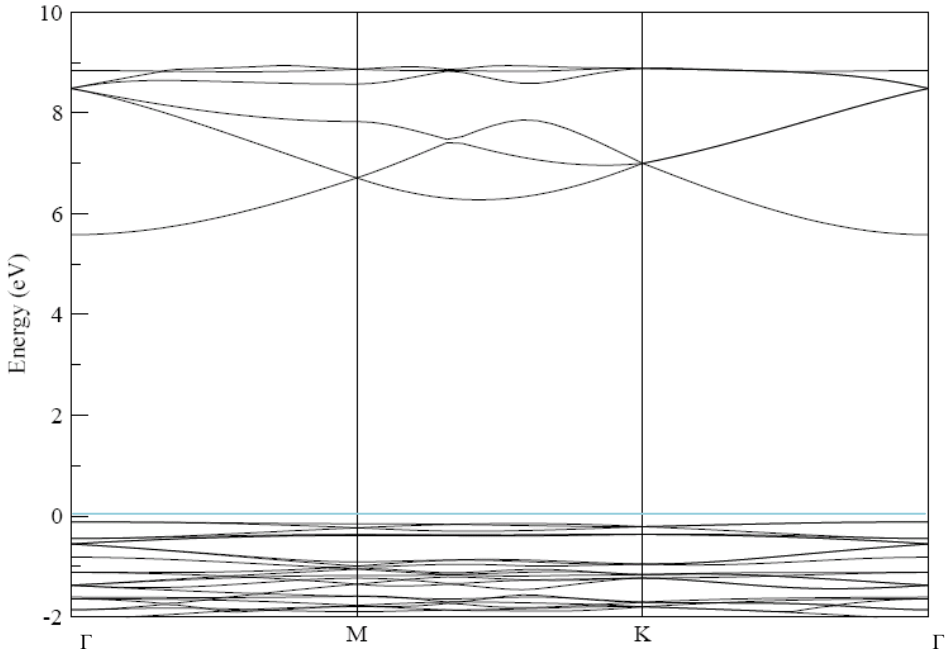


Figure 15: Band structure of α-quartz. Fermi energy is at 0eV.

The band structure we obtained has a direct band gap at Γ of around 5.69 eV. At K the conduction band rises above the band minima by 1.4 eV and at M by 1.1 eV. The

valence bands are pretty flat from Γ to M to K. The band structures as reported in literature vary with different methods of calculation giving different results. While the experimentally observed band gap is 9.65 eV, theory is generally expected to under-predict. A study with pseudopotential method gives a band gap of 6.1 eV from Γ(bottom of CB) to K(top of VB) and 6.44 eV from Γ to Γ. Another parameterised tight binding model gives an 8.4 eV band gap for α-quartz and approx. 7.5-7.2 eVfor amorphous SiO_2.

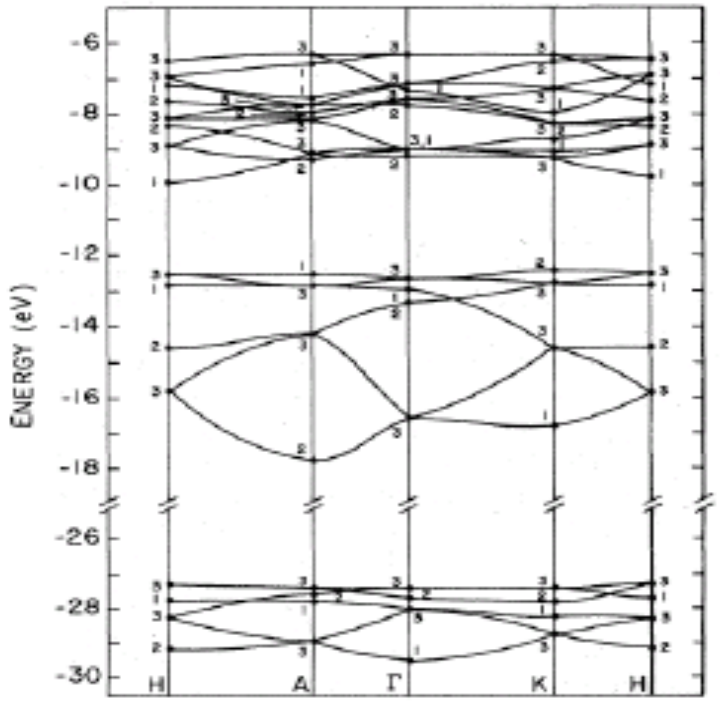


FIG. 2. Valence bands of α-quartz. Computed points are indicated by dots. The energy scale is defined so that the bottom of the conduction band is at zero. In units of $2\pi/a$, Γ is $(0,0,0)$, A is $(0,0,1/2.2)$, K is $(1/\sqrt{3},\frac{1}{3},0)$, and H is $(1/\sqrt{3},\frac{1}{3},1/2.2)$. Note the break in the vertical scale.

Figure 16: Band structure of quartz[1].

[1] Chelikowsky and Schluter, PRB 15 (8), 1977.

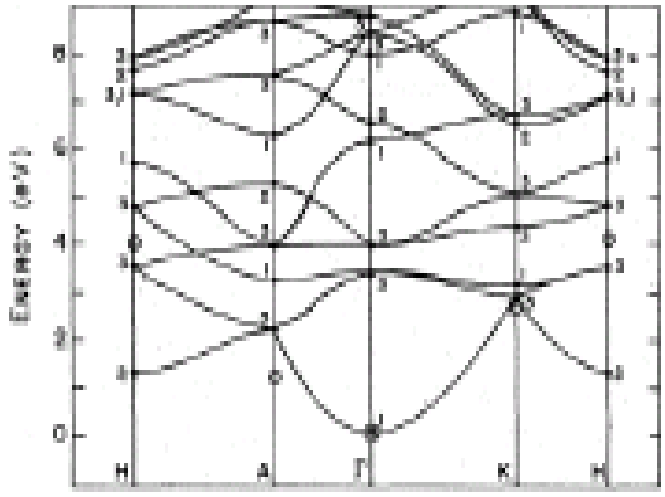


Figure 17: Band structure of quartz[2]. [Lowest conduction bands of α-quartz. Computed points are indicated by dots. Open circles at A, H and K indicate where free-electron bands would intersect these points. The zero of energy is defined as the bottom of the conduction band.]

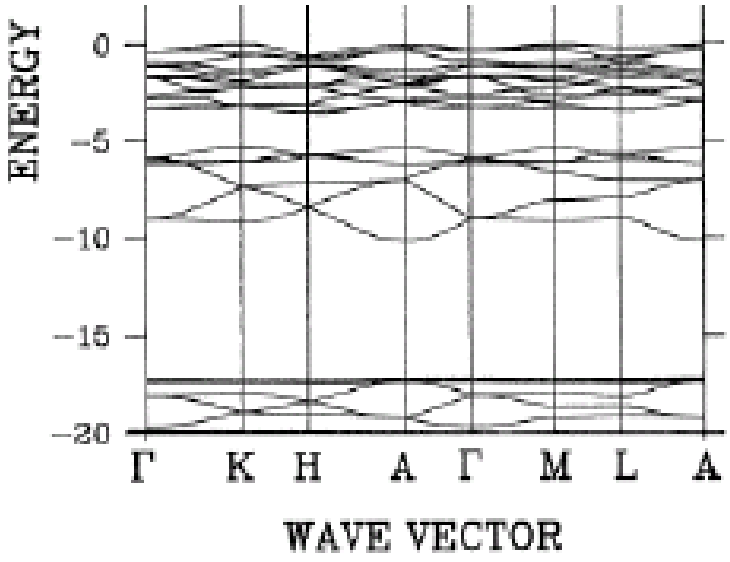


FIG. 1. Calculated band structure of α-quartz.

Figure 18: Band structure of quartz[3].

[2] Phys. Rev. B 18, 2888 -2896 (1978).
[3] PRB 44, 20, 1991: DFT , OLCAO.

A generalized mixed basis method along with tight binding calculations gives a direct band gap at Γ of 6.3 eV. This agrees quite well with our predictions. While a self consistent pseudopotential calculation using wave function ab-initio method, gives the structure and lattice constants are very similar to ours but a band gap from M to Γ of 9.2 eV. A few band structures as shown in literature are included.

The various band structure calculations in literature are too disparate to draw a consistent picture of the band structure of quartz and while ours differs from some of them it also matches up with a few, especially with the Figure 18.

Bulk α-sapphire:

Again we first obtained the band structure for bulk sapphire using DFT (which is shown below) and then compared it with band structure of α-sapphire as described in literature.

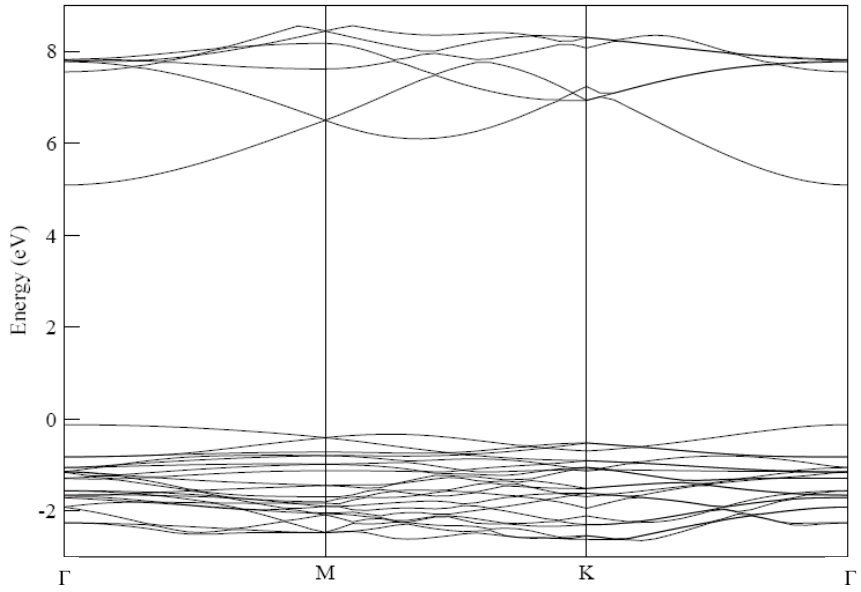


Figure 19: Band structure of sapphire. Fermi energy is at 0 eV.

In our calculations the valence band maximum is clearly at Γ at -0.1208 eV with respect to the Fermi level. The conduction band minimum is also clearly at the Γ point at 5.0902 eV with respect to Fermi energy. So the band gap is 5.211 eV and direct.

We compare this with the band structures described in literature. Experimentally Al_2O_3 is a wide band gap insulator with E_g of 8.3 eVat Γ. DFT calculations using Localised Spherical Wave method (LSW) and LDA show a direct band gap at Γ of 7.1 eV. This agrees with our calculations qualitatively but not quantitatively but we should

remember that their structure also differs as ours is an averaged crystal structure used to obtain a hexagonal surface. A figure depicting this band structure is included below:

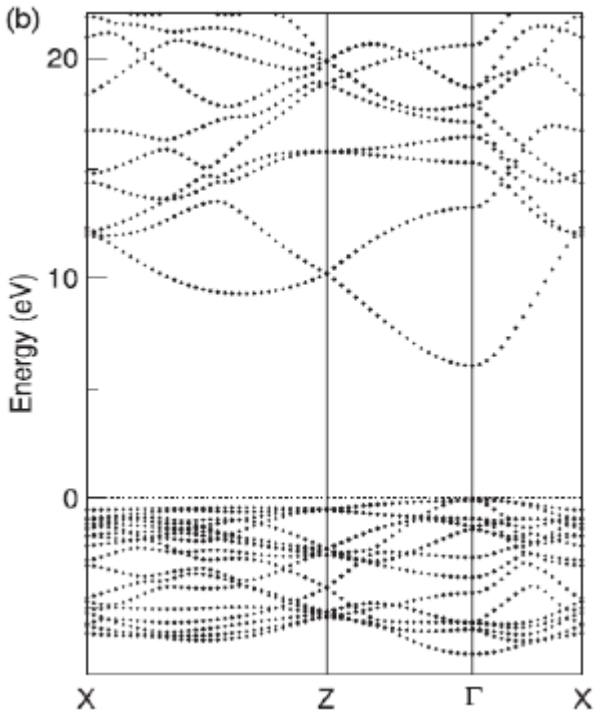


Figure 20: Band structure of sapphire[4].

We thus take it that our calculated band structures for the bulk substrates do give a picture close to reality or at least give as good a description as DFT can provide and use them for further analysis.

[4] J. Phys.: Condens. Matter 19(2007) 386223.

BAND STRUCTURE OF GRAPHENE ON SUBSTRATES:

We now compare the band structure of graphene on substrate with those of free standing mono-layer graphene and the bulk substrate.

Graphene on quartz:

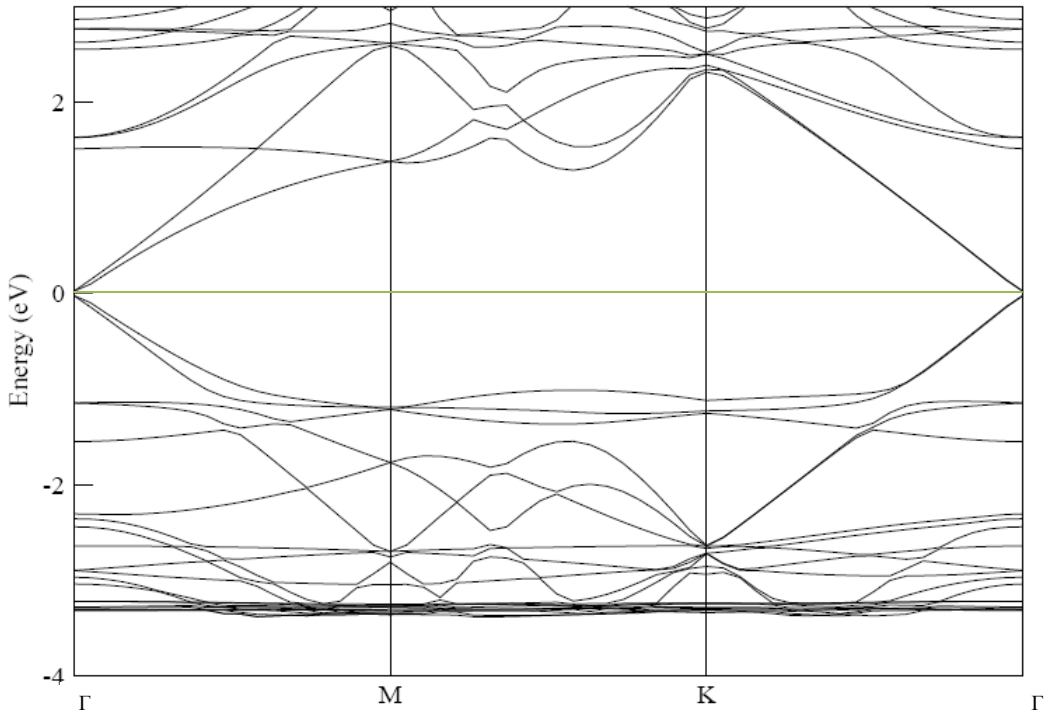


Figure 21: Band structure of graphene on quartz. Fermi energy is at 0 eV.

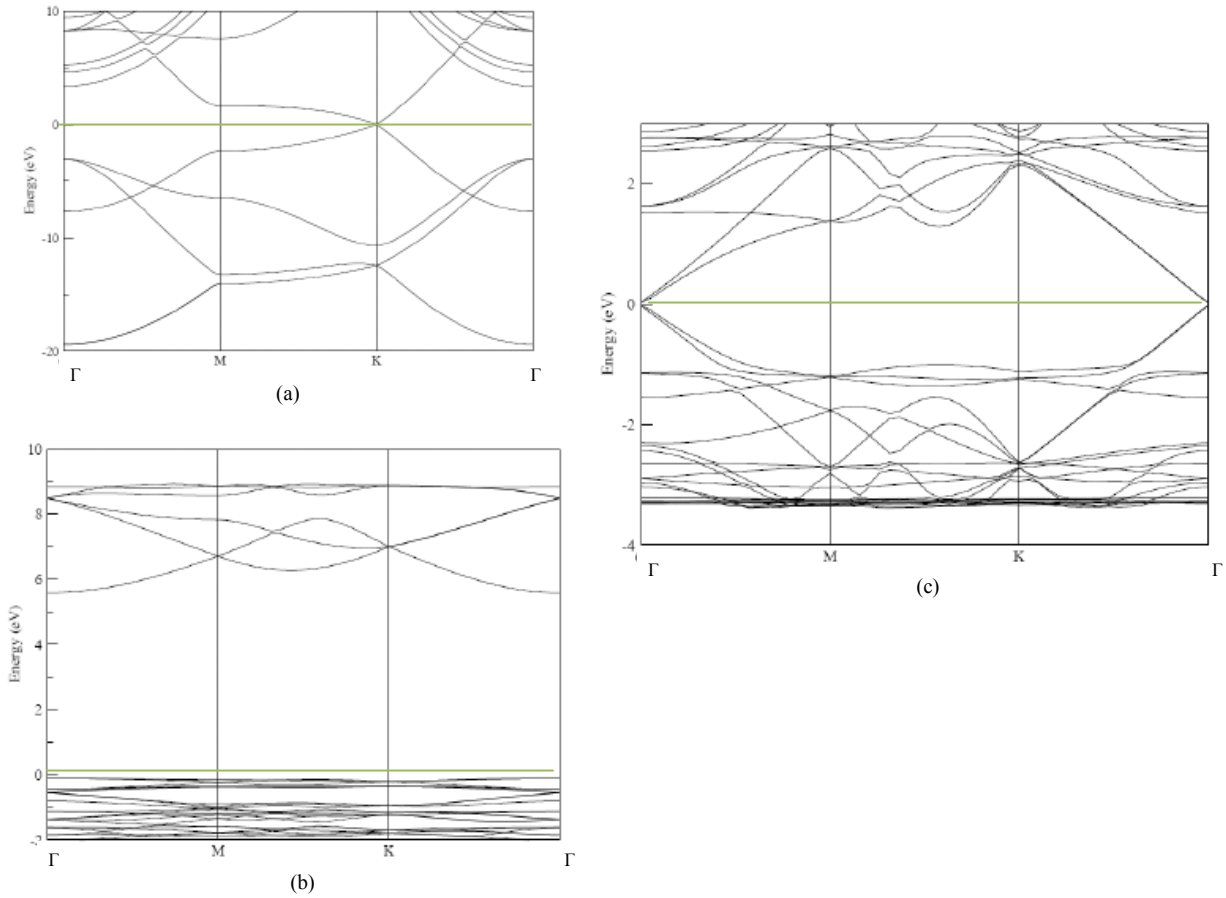


Figure 22: (a) Band structure of mono-layer graphene, (b) Band structure of bulk quartz and (c) Band structure of graphene on quartz. Fermi energy is at 0 eV.

As we study the band structure of our graphene on quartz system we realize that the characteristic linearity of the graphene mono-layer band structure persists. In fact the linearity occurs exactly at the Fermi energy and thus maintains its zero band gap. This tells us that the underlying substrate has not perturbed graphene which is consistent with the picture we got from our positional analysis earlier.

There is however one curious phenomenon. This linear crossing of bands for the graphene plus quartz system occurs at the Γ point instead of the K point, as we would

have expected from graphene. This apparent anomaly however is explained by the symmetry of the underlying substrate and its relation to graphene lattice symmetry.

We carry a detailed examination and comparision of the reciprocal lattice of free standing mono-layer graphene and graphene on quartz. Subsequently we see that the reciprocal lattice structure of the graphene layer on top is a $(2\sqrt{3} \times 2\sqrt{3})R30^{o}$ reconstruction of the reciprocal lattice structure of the quartz below. This implies that the K point of only the graphene mono-layer on top lies on the reciprocal lattice vector of the entire graphene plus quartz system. (Note the K point of the entire system is the same as the K point of the substrate only however it is not the same as the K point of graphene sheet only due to the reconstruction.) It also means that the K point of the graphene monolayer only folds in, by reciprocal lattice symmetry, onto the Γ point of the entire system. Hence we expect the behaviour we would have seen at the K point for graphene only to now occur at the Γ point for the system.

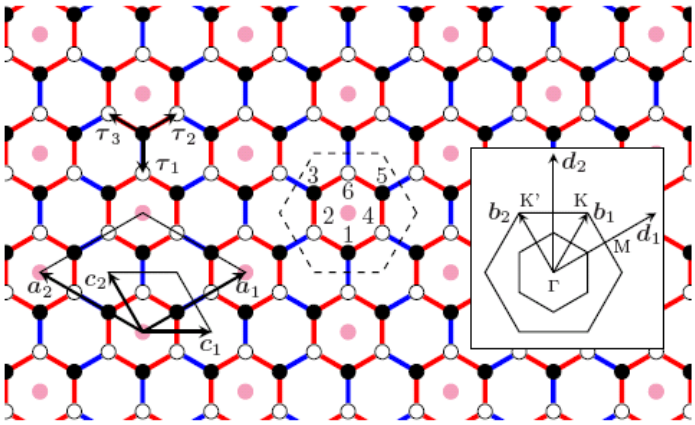


Figure 23: Reciprocal lattice of graphene on Lithium with a (√3 x √3)R30o reconstruction leading to a similar shift in Fermi cone from K to Γ[5]. Refer to paper for more details.

[5] "Energy gap opening in sub monolayer Lithium on graphene", PRB 79, 045417 (2009).

Graphene on sapphire:

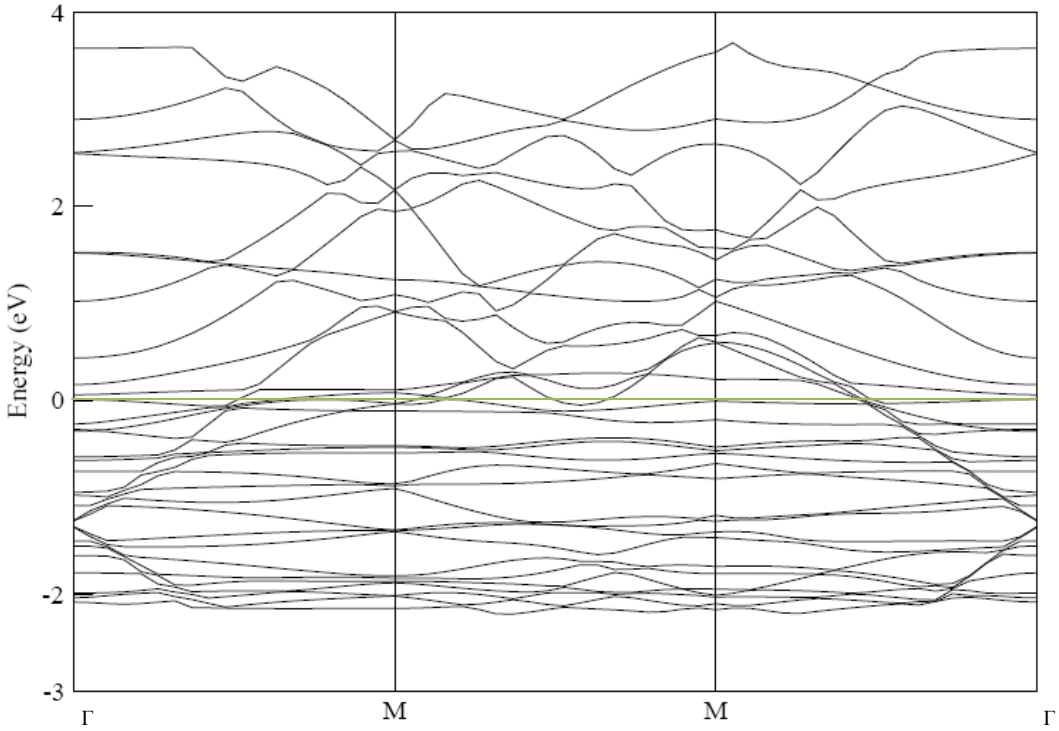


Figure 24: Band structure of graphene on sapphire. Fermi energy is at 0 eV.

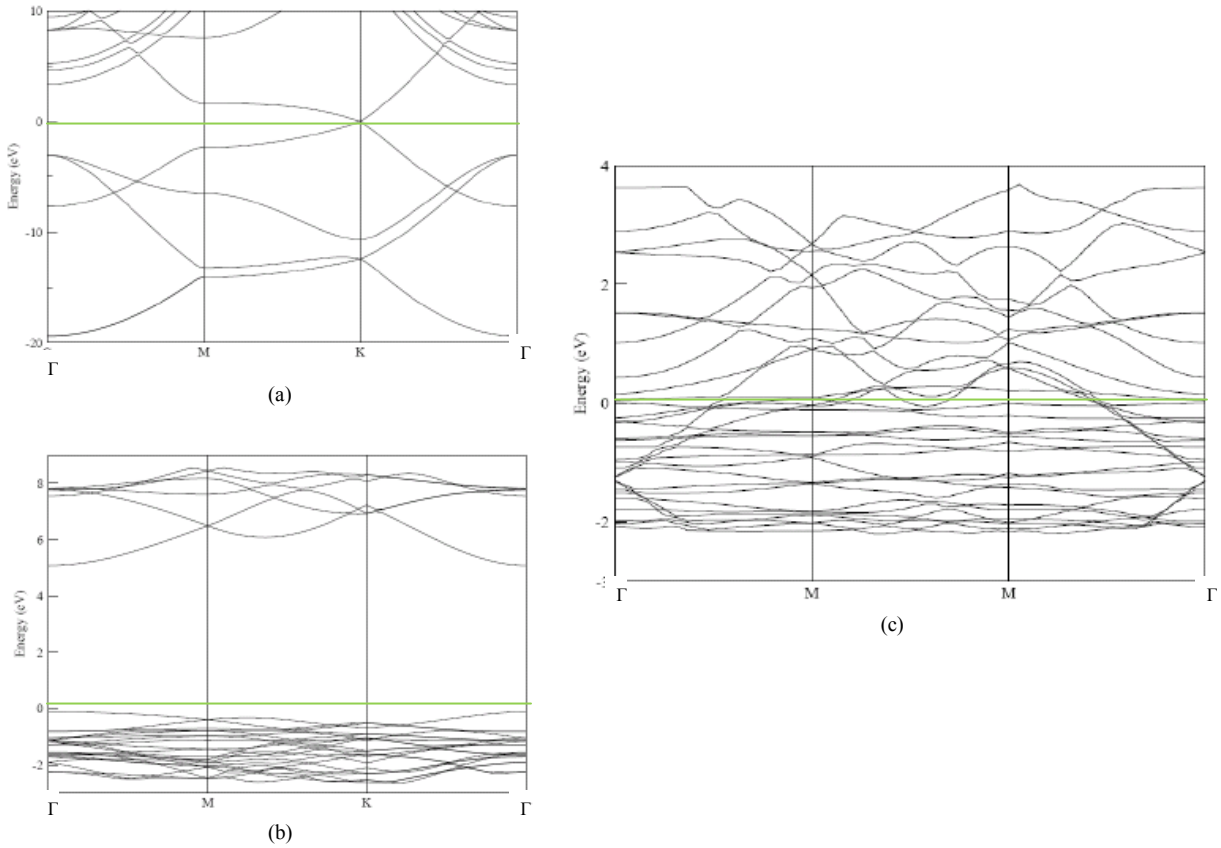


Figure 25: (a) Band structure of mono-layer graphene, (b) Band structure of bulk sapphire and (c) Band structure of graphene on sapphire. Fermi energy is at 0 eV.

Graphene on sapphire has a much more disturbed band structure. The entire system has a metal like band structure with the conduction and valence bands overlapping. It is difficult to obtain much meaningful information from this band structure except that graphene look much more disturbed and might even be bonding somewhat with the substrate in this case.

GRAPHENE AT DIFFERENT DISTANCES:

After looking at the band structure of these relaxed graphene on substrate systems we were somewhat curious as to how the band structures of graphene would look if it were slowly brought close to the substrate and not allowed to relax. This would give us a good idea as to around what distance does graphene lose its characteristic linear behavior. Also it would tell us how much perturbation we see in the relaxed band structures comes from the proximity to substrate and how much comes from rearrangement of C atoms due to relaxation.

So we conducted a study of band structures of non-relaxed graphene plus substrate systems at various distances with 1 nm vacuum.

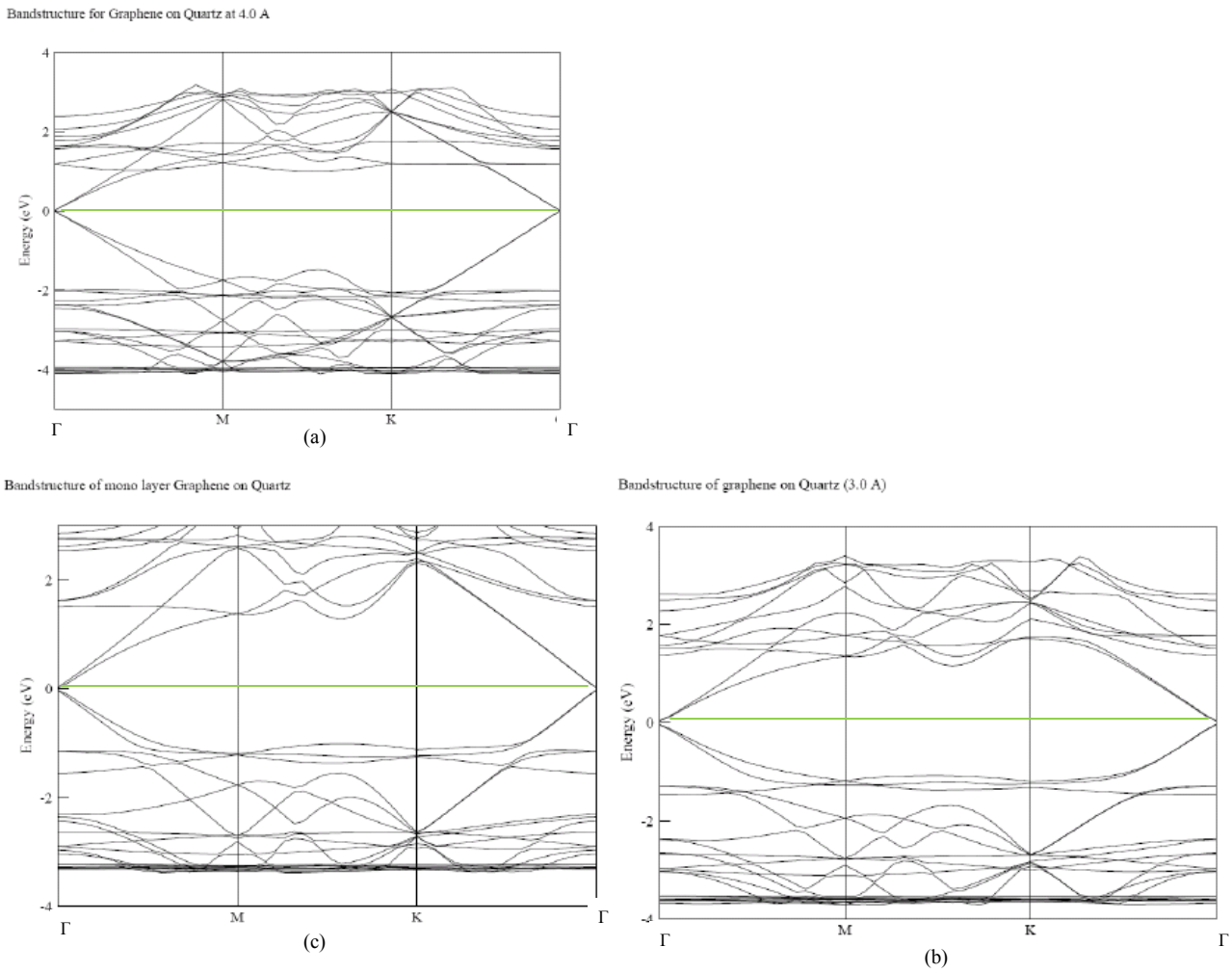


Figure 26: (a) Band structure non-relaxed graphene at 4Å (b) Band structure of non-relaxed graphene at 3Å (c) Band structure of relaxed graphene on quartz at 3Å. Fermi energy is at 0 eV.

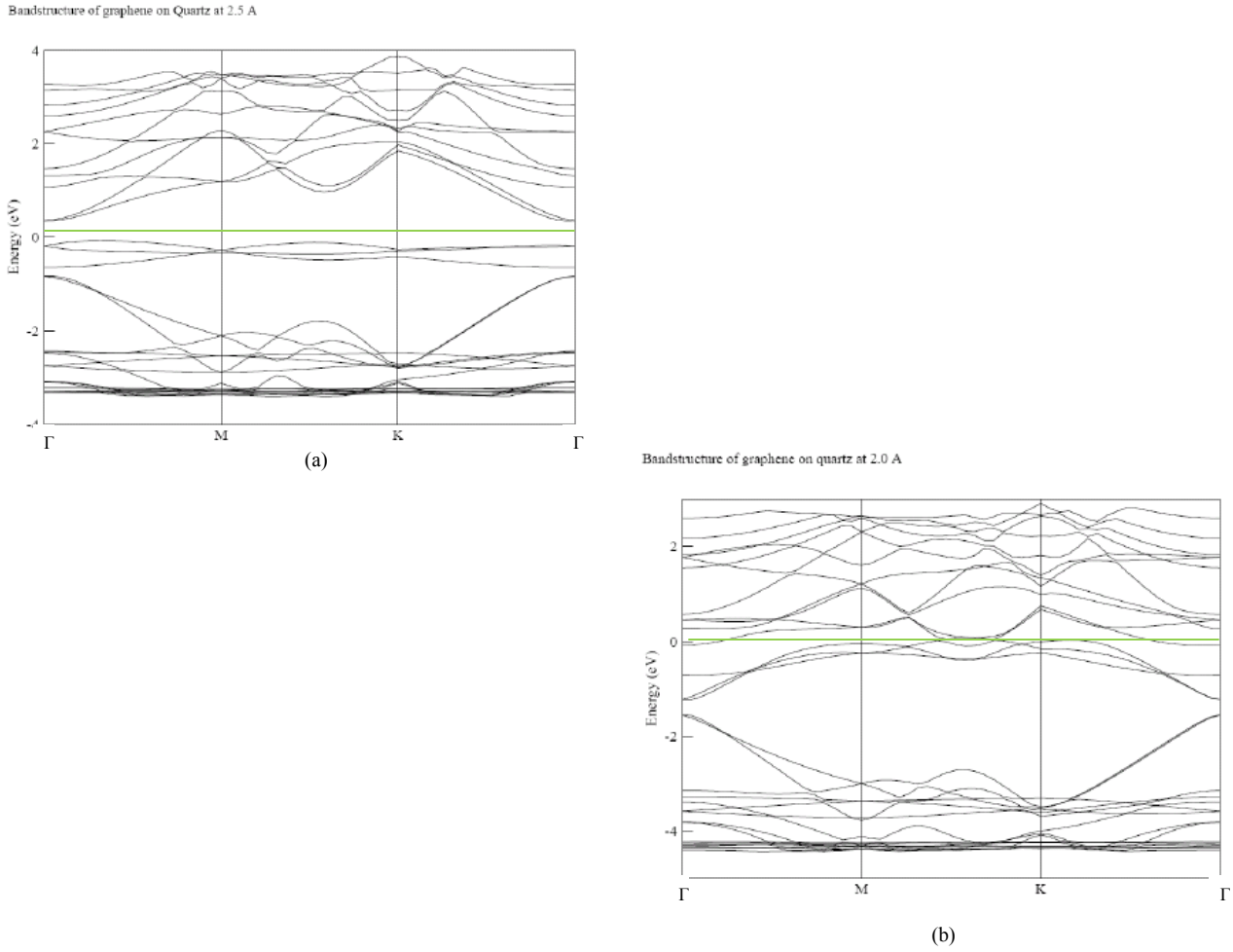
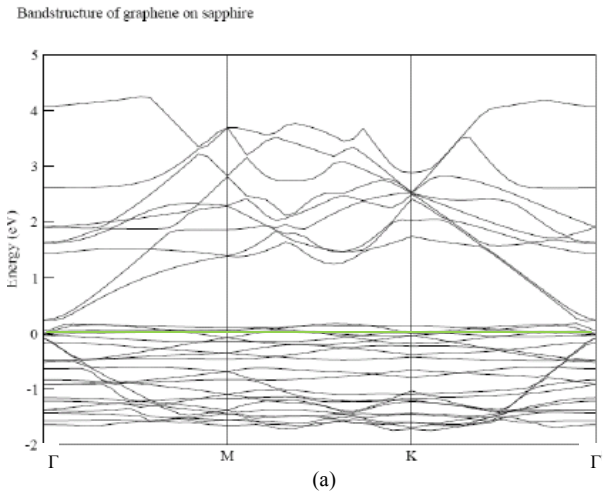
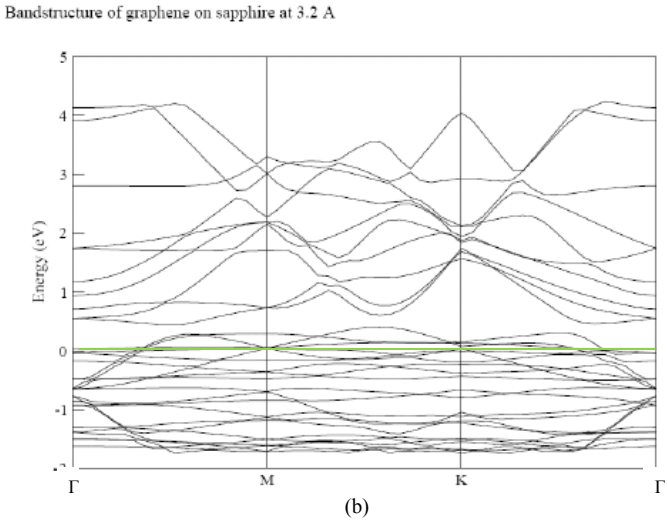


Figure 27: (a) Band structure non-relaxed graphene at 2.5Å (b) Band structure of non-relaxed graphene at 2Å. Fermi energy is at 0 eV.

We can see in how the band structure of graphene progresses from being nicely linear at when it is 4Å away from the substrate to slowly developing a curved nature away from the Fermi level at a 3Å distance. Beyond this graphene comes very close to quartz and its linear structure breaks off to form a gap in a shape that looks surprisingly similar to the band structure of graphene on sapphire. Also to be noted is the resemblance between non-relaxed and relaxed graphene on quartz at 3Å.



(a)



(b)

Figure 28: (a) Band structure non-relaxed graphene at 4Å (b) Band structure of non-relaxed graphene at 3.2Å. Fermi energy is at 0 eV.

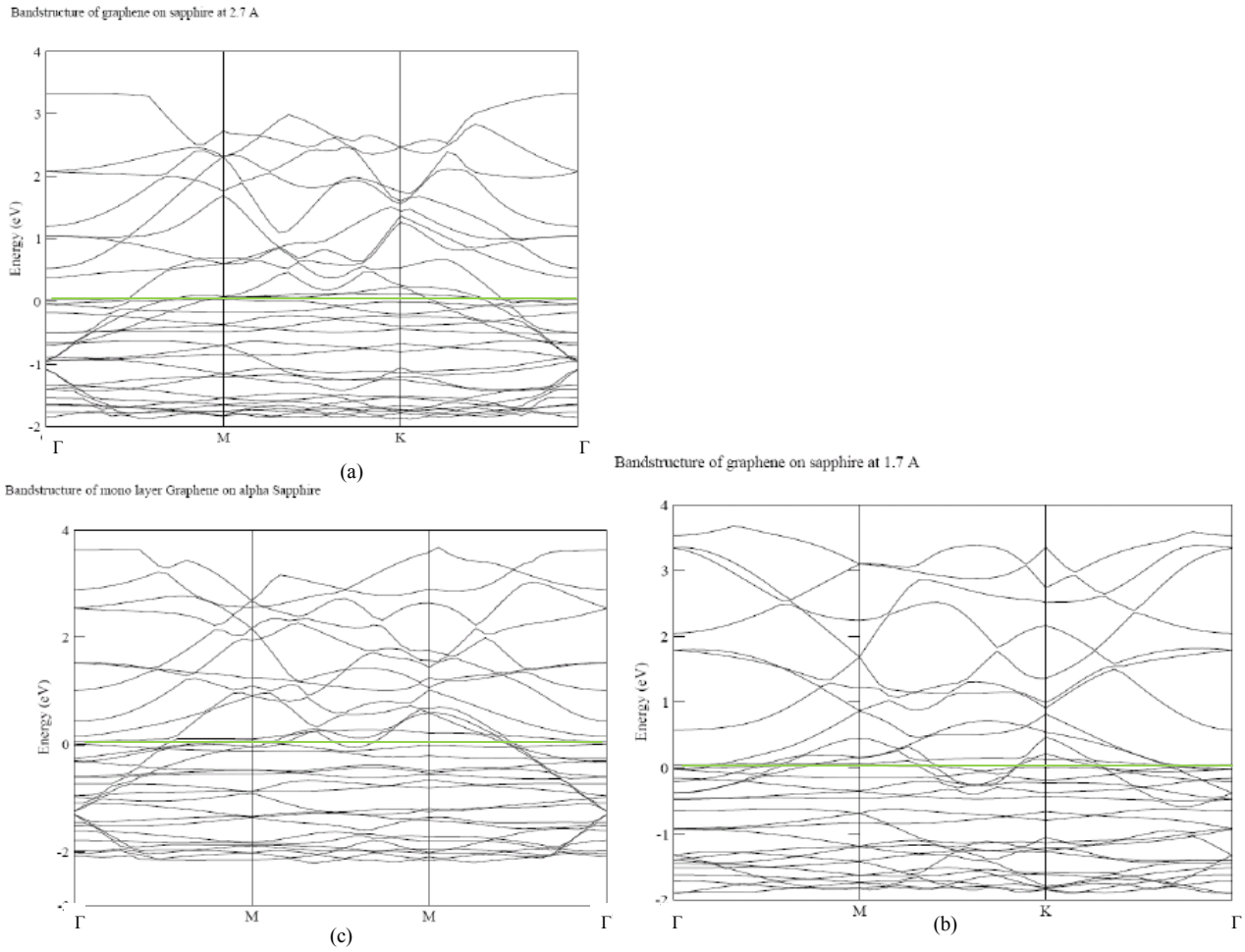


Figure 29: (a) Band structure non-relaxed graphene at 2.7Å (b) Band structure of non-relaxed graphene at 1.7Å (c) Band structure of relaxed graphene on sapphire at 2.7Å. Fermi energy is at 0 eV.

The band structure of non-relaxed graphene on sapphire at 4Å does show some of graphene's linearity at the Dirac point. However in this case graphene is more easily perturbed by Al atoms even at the same distance. Hence the structure deviates from linearity sooner and by the time it comes to 2.7Å distance it is quite a disturbed structure. Again we note that the band structure of non-relaxed graphene at 2.7 Å and our relaxed system (also with a distance of 2.7Å between C and Al) are qualitatively quite similar.

Chapter 6: A Study of the Density of States

We now look at the density of states (DOS) of the substrates and our relaxed structures to get an idea of the energy profile of the states as well as bonding between atoms.

DENSITY OF STATES OF QUARTZ:

Below are figures showing the Total DOS for quartz as well as DOS projected on one atom and its valence orbitals. Since we are dealing with bulk structures here any Si or O atom is equivalent to any other.

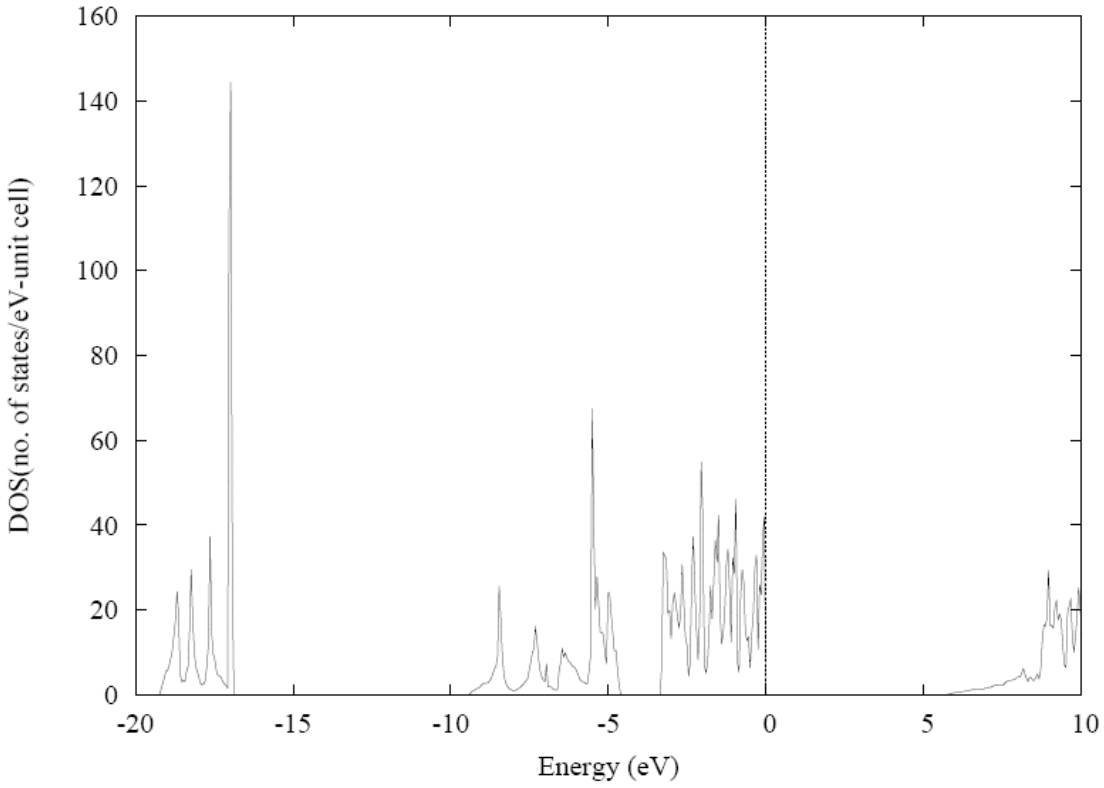


Figure 30 : Total DOS for quartz. Fermi energy is at 0 eV.

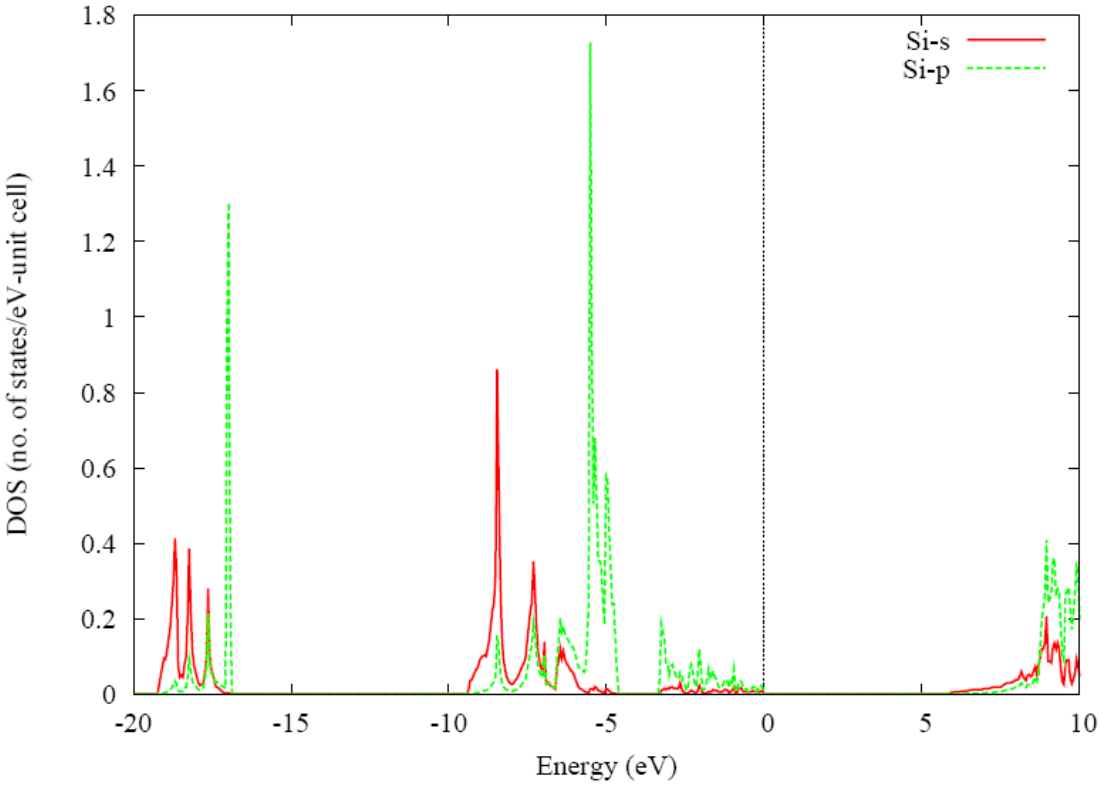


Figure 31 : Site and orbital projected DOS for a Si atom in bulk quartz. Fermi energy is at 0 eV.

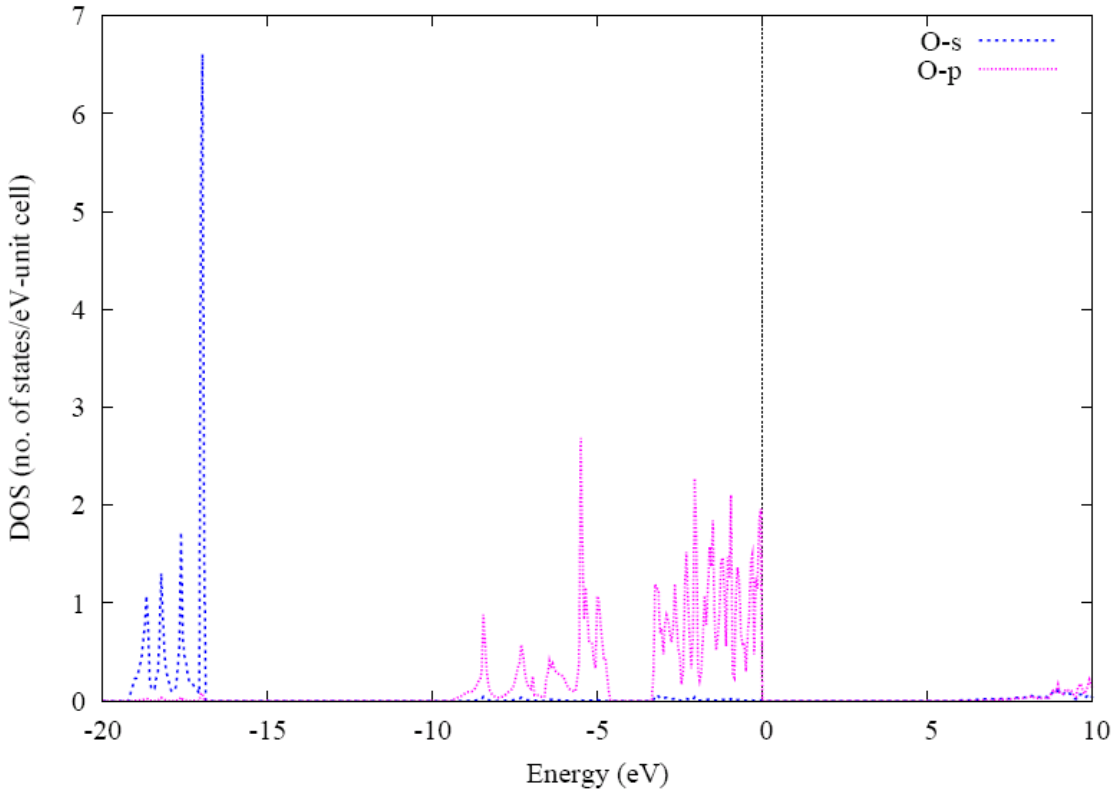


Figure 32 : Site and orbital projected DOS for a O atom in bulk quartz. Fermi energy is at 0 eV.

Comparing the plots we obtained with literature we find that there is a good match in terms of trends though the actual energy values vary.

In our case lower -19 to -17 eV is occupied by Si. The valence band around Fermi level is more dominant in Si-p than Si-s. The valence band has a dominant O character with the band between -19 eV and -17 eV being predominantly O-s and the one close to the Fermi level, between -10 and 0 eV more like O-p.

Then there is a band gap after which the conduction band is pretty much Si-s and O-s initially and then Si-p and O-p later on. The conduction band has some O character too though much more O-p than O-s.

GRAPHENE ON QUARTZ:

We now look at the DOS for our relaxed graphene on quartz system.

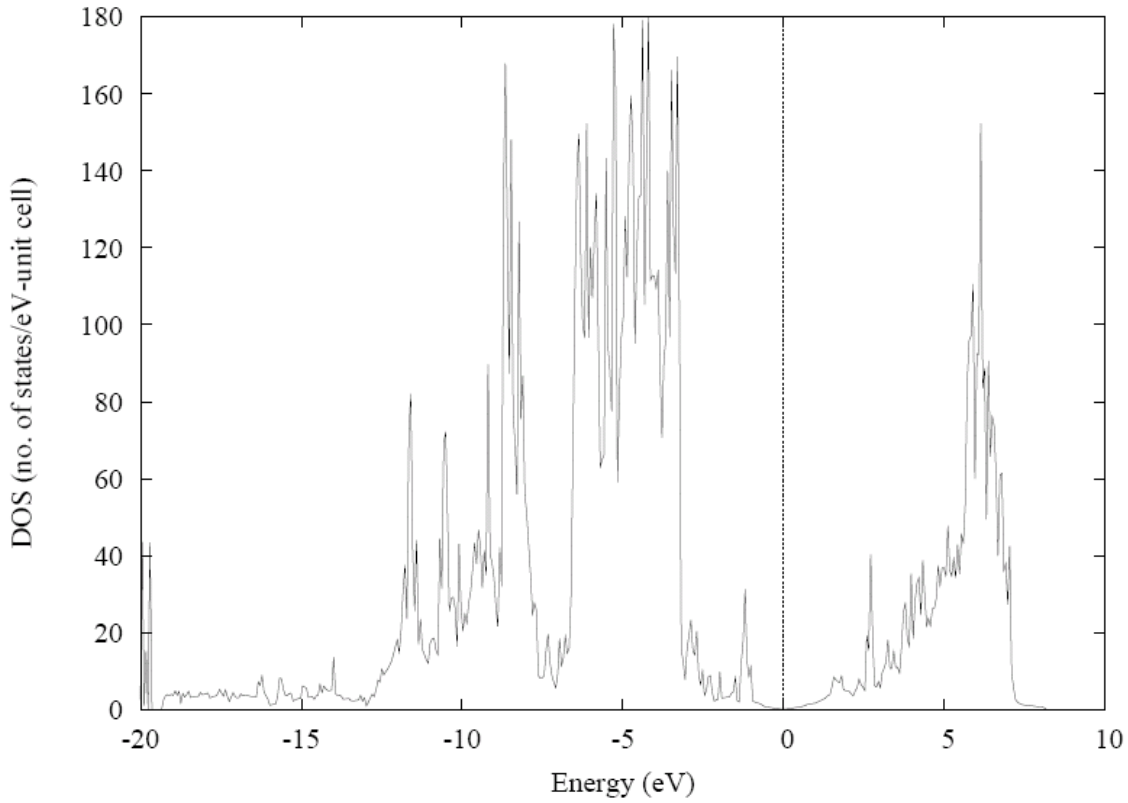


Figure 33 : Total DOS for graphene on quartz. Fermi energy is at 0eV.

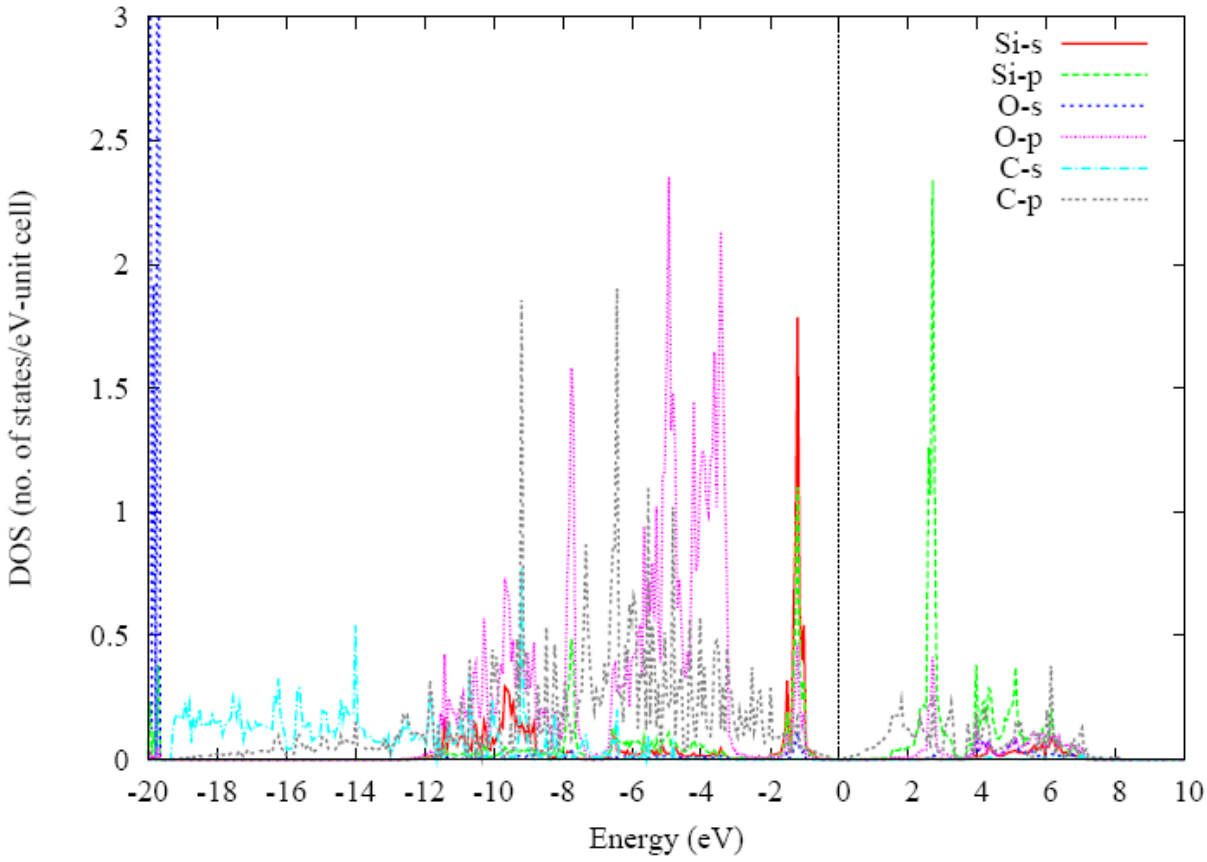


Figure 34 : Site and orbital projected DOS for Si and O atoms in their top most layers a C atom in graphene on quartz. Fermi energy is at 0eV. O-s is cut off but goes upto 6.2 states/eV-unit cell.

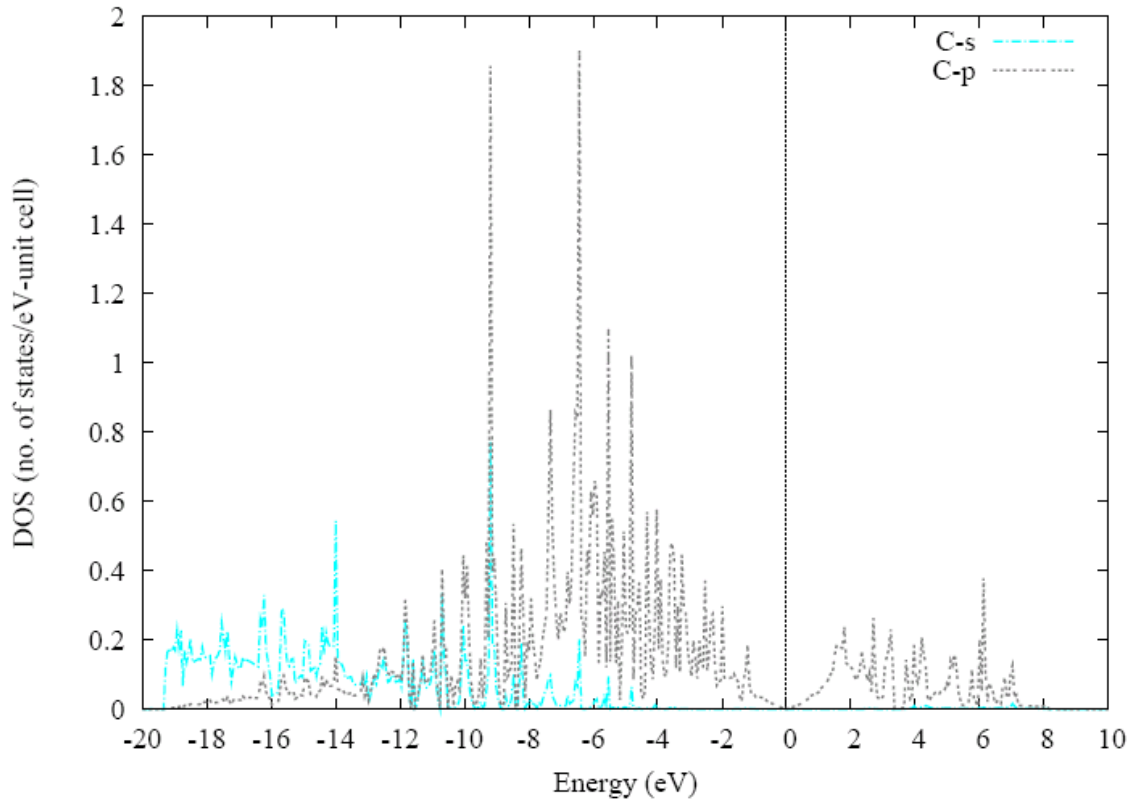


Figure 35 : Site and orbital projected DOS for a C atom in graphene on quartz. Fermi energy is at 0ev.

As we can see the VB of our structure seems to be divided into bands. The region around -20 eVis O s type and O s seems confined around the area. -20 to -10 eV are primarily C-s and C-p. Around -12 eV to 8 eV in the band is an overlap of C-s, C-p, Si-s, O-p and some small amount of Si-p.

The next area in the VB from -6eV to -3eV is dominated by C-s and O-p and very small amount of C-s, Si-s and Si-p. Just below the Fermi level around -2 eV Si-s peaks up, there is some C-p, O-s, O-p, Si-p. In the VB around 2 eV we get a hybridization of C-p, large amount of Si-p, O-p, and as we go higher O and Si s character that comes in.

At the Fermi level there is a very small presence of C-p only but otherwise a gap. This is very similar to the DOS expected from a free standing graphene monolayer which tells us we should expect linearity in the band structure and very little bonding between graphene and substrate, if any. This is consistent with the band structure plots we obtained earlier.

DENSITY OF STATES OF SAPPHIRE:

We now look at the DOS for sapphire and compare it with literature.

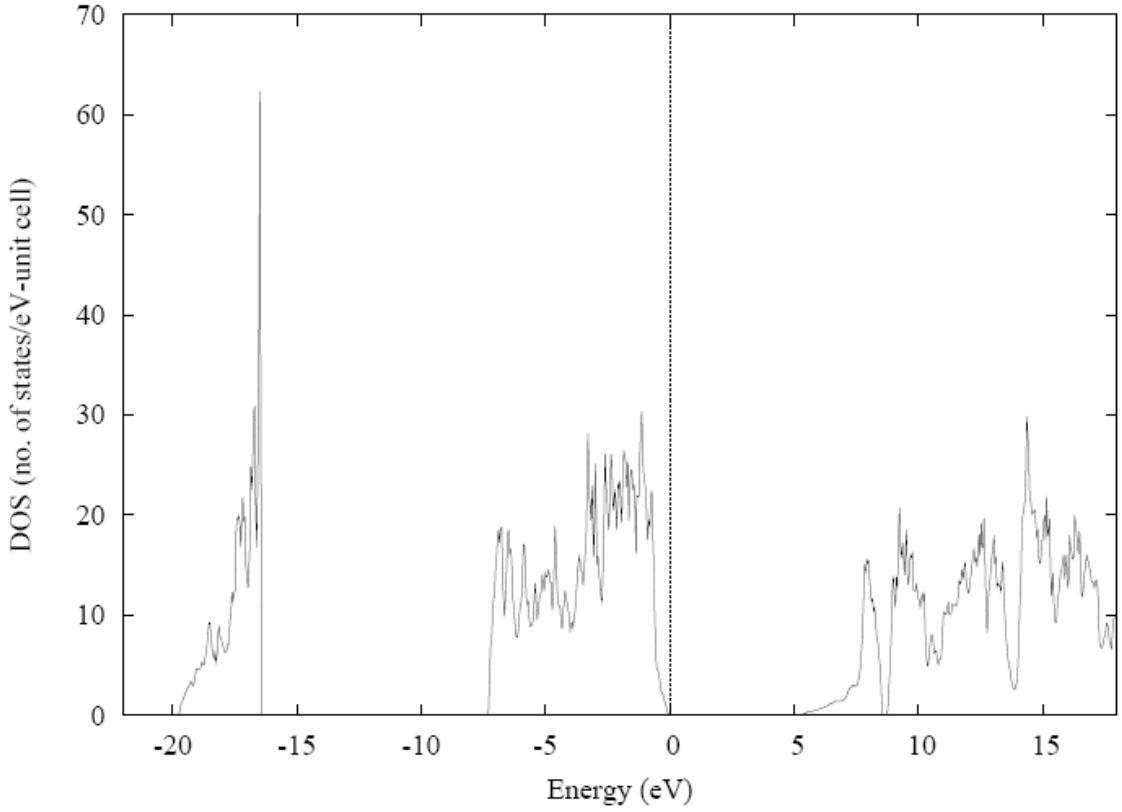


Figure 36 : Total DOS for sapphire. Fermi energy is at 0 eV.

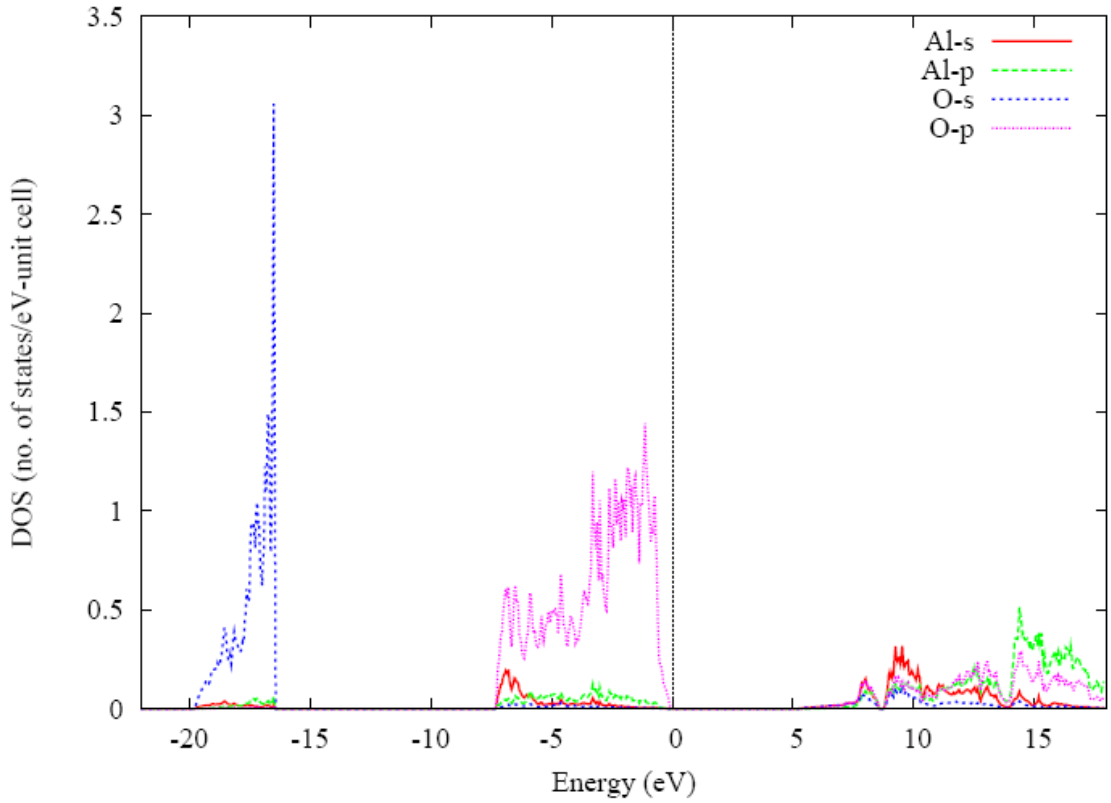


Figure 37 : Site and orbital projected DOS for a Al and O atoms in sapphire. Fermi energy is at 0 eV.

Here we observe the CB and VB are divided into very obvious bands. Between -20 to -16 eV the region is primarily O-s with some Al s and p. Between -7.5 eV and the Fermi level it is mainly O-p with some Al-s and Al-p and O-s. Then there is a big band gap till around 6 eV where the CB is an overlap of all 4 orbitals Al and O s and p. This observation seems to match very well with literature.[6]

[6]PRB, 56, 7277-7284, Xu, Gu, Ching(1997)

GRAPHENE ON SAPPHIRE:

Subsequently we take a look at the DOS for our relaxed system on graphene on sapphire.

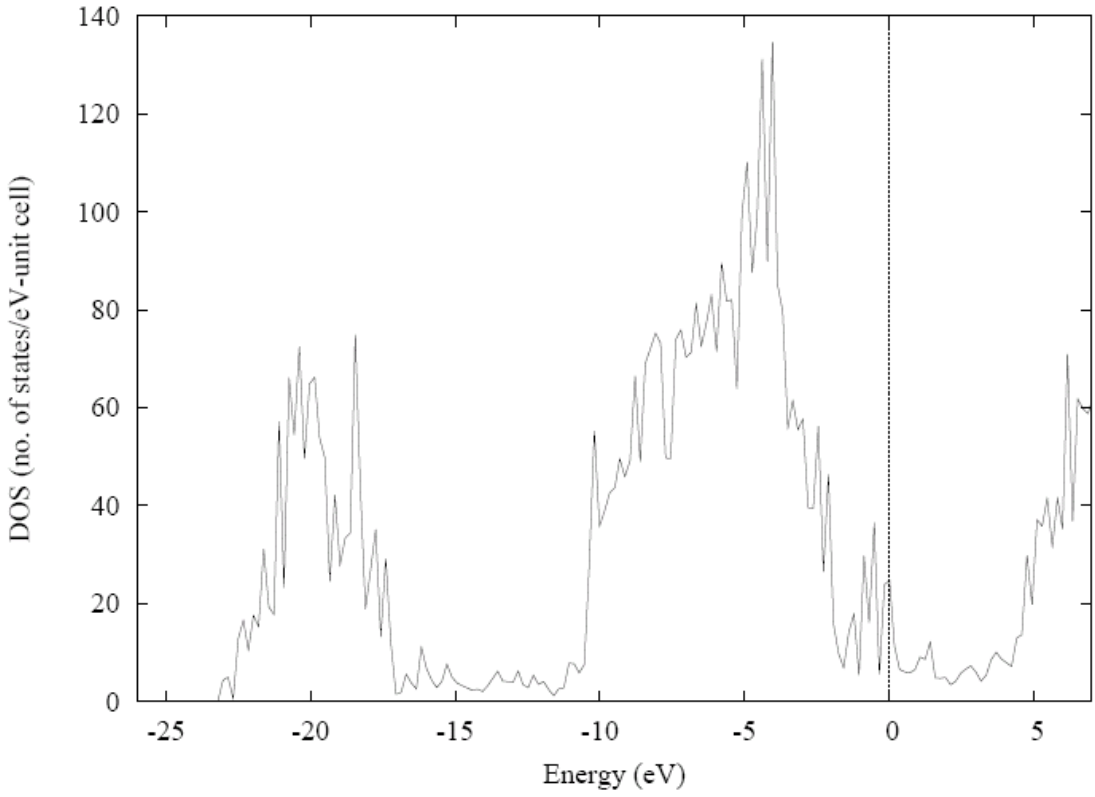


Figure 38 : Total DOS for graphene on sapphire. Fermi energy is at 0 eV.

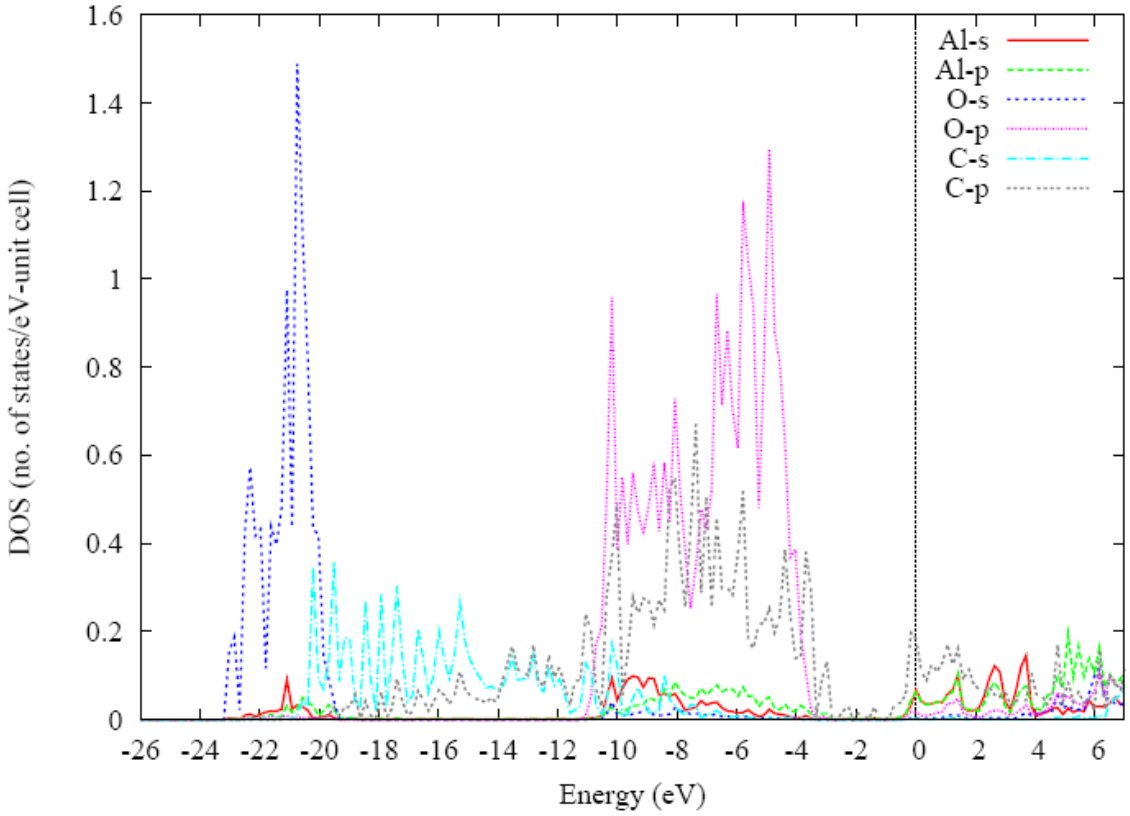


Figure 39: Site and orbital projected DOS for Al and O atoms in their top most layers and a C atom in graphene on sapphire. Fermi energy is at 0 eV.

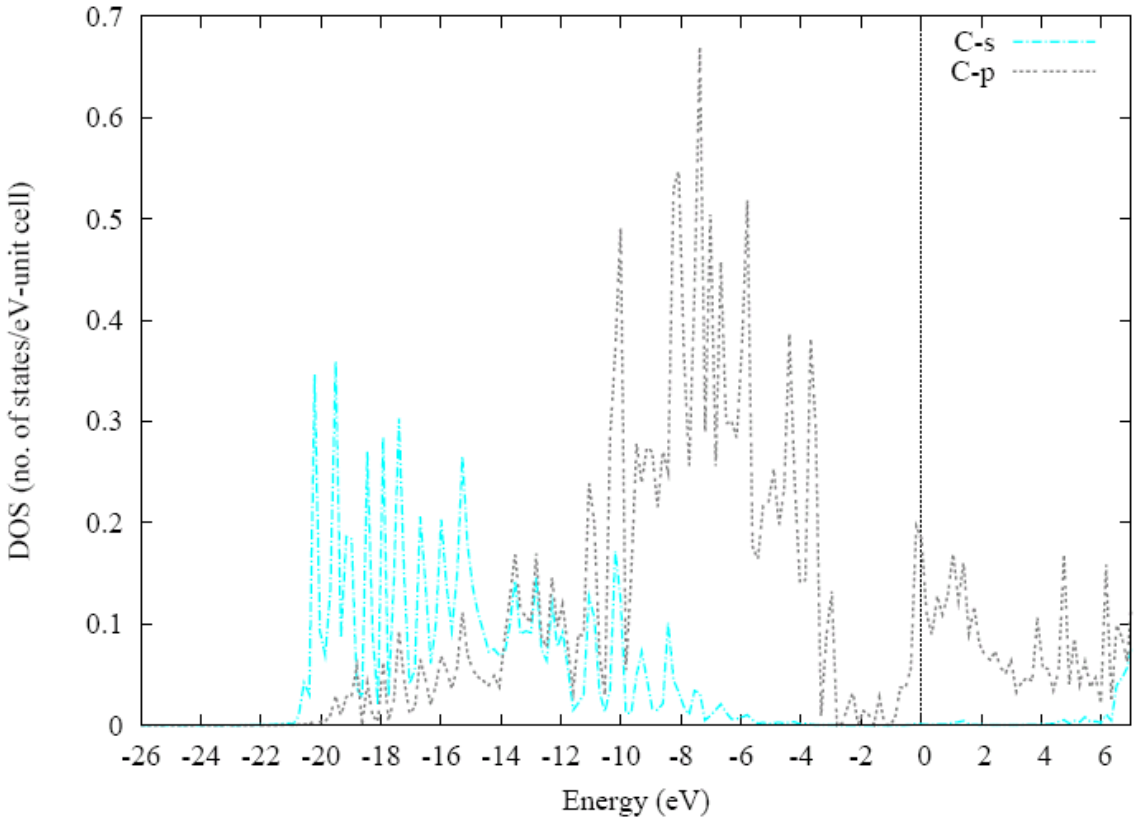


Figure 40 : Site and orbital projected DOS for a C atom in graphene on sapphire. Fermi energy is at 0 eV.

Again here the O-s seems to be confined to the lower part of the VB. This is between -23 eV and -19 eV and made up of O-s and some Al-s, Al-p and O-p. Then the C region begins with both C-s and C-p spread between -22 and -10 eV. In the lower band of CB there is hybridization between C-p and O-p mainly, with some Al-s and Al-p and O-s.

The region near the Fermi level is made up of some states of C-p along with Al-s, Al-p some O-p, O-s and very little C-s. Beyond 4 eV the Al-s drops and Al-p increases along with O-s and O-p.

In this case, as against the quartz case, there is some bonding between C-p (which mainly forms the C states near Fermi level for graphene) and Al-s and Al-p. Thus we do expect a deviation from the linear band structure of free standing graphene as well as a smaller distance between graphene and sapphire than what we see between graphene and quartz. All this is consistent with our earlier observations.

Chapter 7: Binding Energy and Charge Density

We will now take a look at some more analysis done on the graphene on substrate structures.

BINDING ENERGY:

In order to get a better idea of the bonding of the graphene layer to the substrate we carried out binding energy calculations. This entails taking the total energy of our relaxed graphene on substrate structure and from that subtracting the total energies of relaxed graphene sheet and relaxed substrate individually. For this the graphene on substrate unit cell was separated into two parts, the part with only graphene and the part with only the substrate. Then we allowed the position of atoms in these new isolated unit cells to relax till their energies converged. Then the total energies were subtracted out as explained before. The formula we used was:

$$E^{Tot}_{binding} = \frac{E^{Tot}_{relaxed\ graphene\ on\ substrate} - E^{Tot}_{relaxed\ substrate\ only} - E^{Tot}_{relaxed\ graphene\ only}}{Total\ no.of\ atoms\ in\ unit\ cell}$$

The results were as follows:

Graphene on quartz:

The binding energy was 0.017442eV/atom approximately. Although this binding energy is positive, it is a very small amount which means that graphene is neither attracted to nor repelled by quartz.

Graphene on sapphire:

The binding energy was -3.5766 eV/atom approximately. This is a negative binding energy which means graphene tends to stick to sapphire surface.

CHARGE DENSITY:

We also plotted the charge densities of graphene on the substrate for our relaxed structures.

Graphene on quartz:

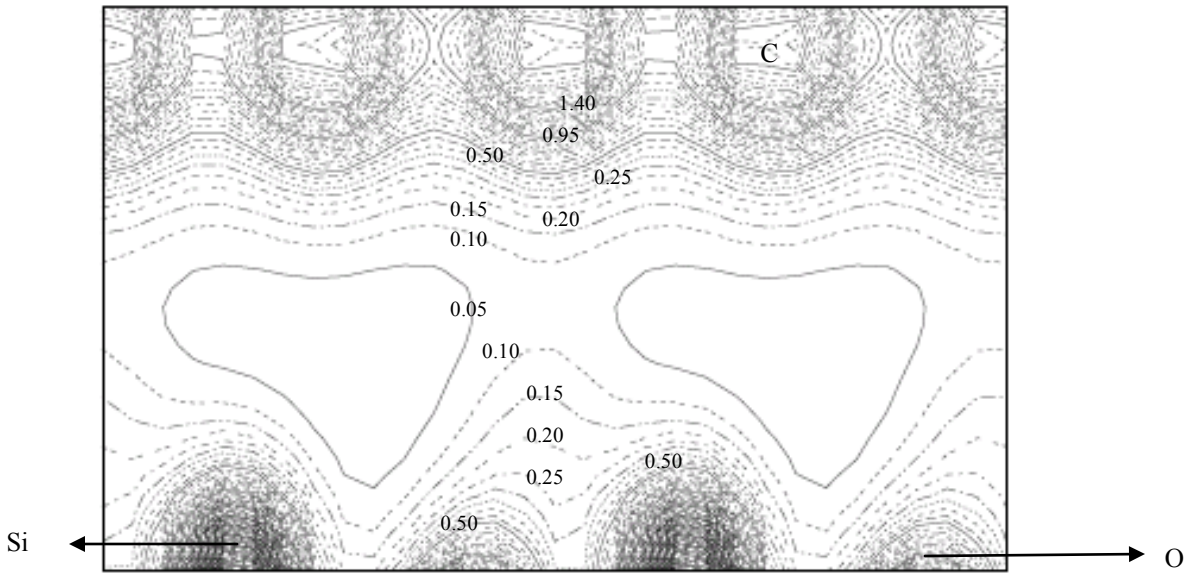


Figure 41 : Charge density plot for graphene on quartz. The various contours of charge density are shown and their values are given in no. of electrons/Å^2

As we can see there is a big distance between the C and top most layer of Si atoms. There is also very little charge density in that region which fits in well with our conclusion that graphene does not get perturbed by quartz with a Silicon top layer.

Graphene on sapphire:

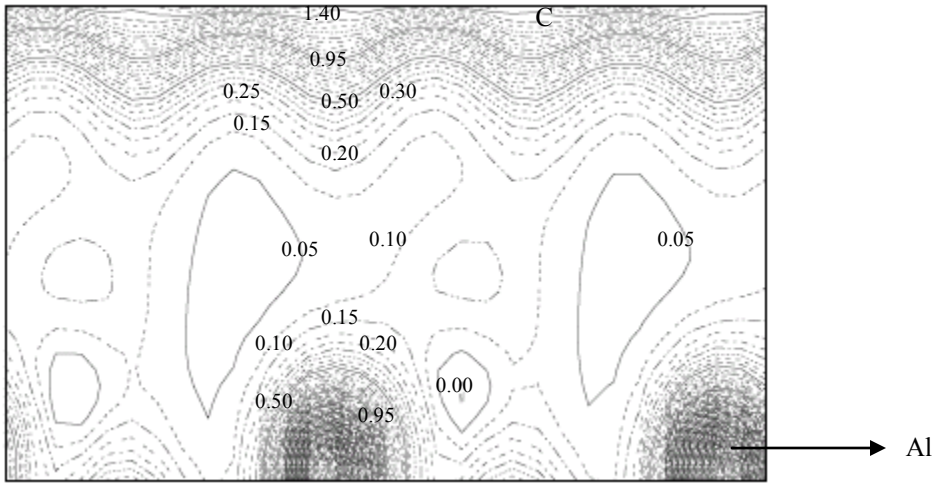


Figure 42 : Charge density plot for graphene on sapphire. The various contours of charge density are shown and their values are given in no. of electrons/Å^2

This figure is not very conclusive as we cannot day for sure that there is or is not any charge exchange between the carbon layer and the topmost Aluminium layer.

Chapter 8: Conclusions and Further Work

Thus we conducted a DFT study of graphene mono-layer on α-quartz and α-sapphire. In our structures the quartz was Si terminated and sapphire was Al terminated i.e. the top most layer of the substrate was made up of Si or Al atoms respectively.

We concluded that on quartz, while the graphene layer is not perturbed it also does not bond to the surface and it retains its zero bandgap. On sapphire however, it comes close to the surface and may or may not bond with it but its bandstructure gets highly perturbed. In fact the bandstructure of graphene on Al-terminated sapphire looks like that of a metal. Both these configurations are not very useful to us.

In the future, we intend to look at the structure and properties of oxygen-terminated quartz and sapphire, i.e. the top most layer in our structures would be a layer of Oxygen atoms. Along with that, if we see the substrate perturbing the graphene too much, like we see in the case of graphene mono-layer on Al-terminated sapphire, we will undertake a study of bi-layer graphene on that substrate.

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